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# ON THE VARIATION OF LATITUDE AT DEHRA DŪN.

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*(From the Survey of India, Dehra Dūn.)*

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

During the years 1930–33, a series of Latitude observations by the Talcott method was carried out at the Dehra Dūn Observatory utilizing the well-known chain method. The observations are described in *Survey of India Geodetic Reports.*[1]

The object of this paper is to discuss the diurnal and annual terms in the variation of latitude at Dehra Dūn comparing them with the corresponding terms at the other stations, and also to outline the progress made in the solution of this problem in recent years. The above observations have also been utilized to test the variation of latitude with moon's age, which has often been suggested.

Before proceeding further, it would be well to say a few words about the merits and demerits of the chain method. It can easily be verified that an error in zenith distance and time has least effect on the determination of latitude $\phi$, when the star is at transit. In this position, $d\phi = d\delta$, hence in the Talcott method, an error in declination $\delta$ enters fully in $\phi$. It is a well-known fact that the apparent places of stars as deduced from different catalogues are very discrepant. There are also systematic errors of declinations in different right ascensions. In utilizing the observational material for research on the variation of latitude, it is not nearly accurate enough to take declinations from the catalogues.

It appears then at first sight that the method of observation should be such that the observed latitude is practically independent of the declinations of stars used. The only good method, which satisfies this condition is, observation of a circumpolar star at both its transits. But this method has its own difficulties, and it is not proposed to go into them in this paper.

The chain method utilises Talcott pair observations, and is supposed to determine relative errors of declinations of the stars used. The 24 hours of right ascensions are divided into a convenient number of groups. At Dehra on the advice of the Astronomer Royal, six groups were taken, each group

(consisting of about 8 or 9 Talcott pairs) extending approximately over 4 hours of right ascension. These groups are observed by pairs, one before midnight and one after, each group pair lasting for about two months.

Table I shows the right ascensions and the periods of observation of each pair during the three years of observation.

TABLE I.

| Group-pair | R. A. | Mean R. A. | Year | | |
|---|---|---|---|---|---|
| | | | 1930—31 | 1931—32 | 1932—33 |
| | h. m. s. | h. m. s. | | | |
| $1_e$, $2_m$ | 9 06 07·2<br>13 30 46·7 | 11 18 27·0 | (2, 3) Feb. to (6, 7) April | (19, 20) Feb. to (14, 15) April | (4, 5) Feb. to (8, 9) April |
| $2_e$, $3_m$ | 13 30 46·7<br>16 59 14·1 | 15 15 00·4 | (13, 14) April to (30, 31) May | (20, 21) April to (22, 23) May | (12, 13) April to (1, 2) June |
| $3_e$, $4_m$ | 16 59 14·1<br>19 59 58·2 | 18 29 36·2 | (5, 6) June to (8, 9) Aug. | (27, 28) May to (16, 17) Aug. | (4, 5) June to (25, 26) July |
| $4_e$, $5_m$ | 19 59 58·2<br>23 31 36·8 | 21 45 47·5 | (15, 16) Aug. to (10, 11) Oct. | (16, 17) Aug. to (11, 12) Oct. | (9, 10) Aug. to (4, 5) Oct. |
| $5_e$, $6_m$ | 23 31 36·8<br>4 03 17·7 | 1 47 27·3 | (1, 2) Oct. to (28, 29) Nov. | (22, 23) Oct. to (3, 4) Dec. | (10, 11) Oct. to (1, 2) Dec. |
| $6_e$, $1_m$ | 4 03 17·7<br>9 06 07·2 | 6 34 42·5 | (2, 3) Dec. 1930 to 5th Feb. 1931 | (8, 9) Dec. 1931 to (29, 30) Jan. 1932 | (7, 8) Dec. 1932 to (8, 9) Feb. 1933 |

It will be seen, that each group is observed for about four months. During two months, it is the earlier of the two groups forming the pair, and is denoted by the suffix $e$ (evening), and during the other two months, it is the later, and is denoted by the suffix $m$ (morning).

Let $1_e$, $1_m$ be the mean latitudes deduced from morning and evening observations of group 1, and let

$$(1_e - 2_m) + (2_e - 3_m) + \ldots + (6_e - 1_m) = C \qquad \cdots \quad (1)$$

This closure error C has been the subject of several discussions. It would be zero, if latitude remained constant during the course of a night and if there were no errors of observation. If it could be assumed, that C was due to accidental errors, then by distributing it equally amongst the various group differences, we should get a good determination of the relative errors

of adopted mean declinations of each group-pair. These group differences were determined at Dehra Dūn for 3 years, and are shown in Table II.

TABLE II.

*Group Differences.*

| | 1930–31 | 1931–32 | 1932–33 | Mean | Adjusted |
|---|---|---|---|---|---|
| $1_e$—$2_m$ | +0·13 | +0·30 | +0·32 | +0·25 | +0·27 |
| $2_e$—$3_m$ | +0·11 | +0·01 | −0·07 | +0·02 | +0·04 |
| $3_e$—$4_m$ | −0·15 | −0·14 | −0·03 | −0·11 | −0·10 |
| $4_e$—$5_m$ | −0·13 | +0·07 | +0·01 | −0·02 | 0·00 |
| $5_e$—$6_m$ | −0·14 | −0·28 | −0·07 | −0·16 | −0·15 |
| $6_e$—$1_m$ | −0·07 | −0·07 | −0·08 | −0·07 | −0·06 |
| C | −0·25 | −0·11 | +0·08 | −0·09 | 0·00 |

Using mean values of these differences, the values of latitude as determined by different groups are reduced to the first group, and are thus made into a homogeneous whole. The resulting values of latitude should then be

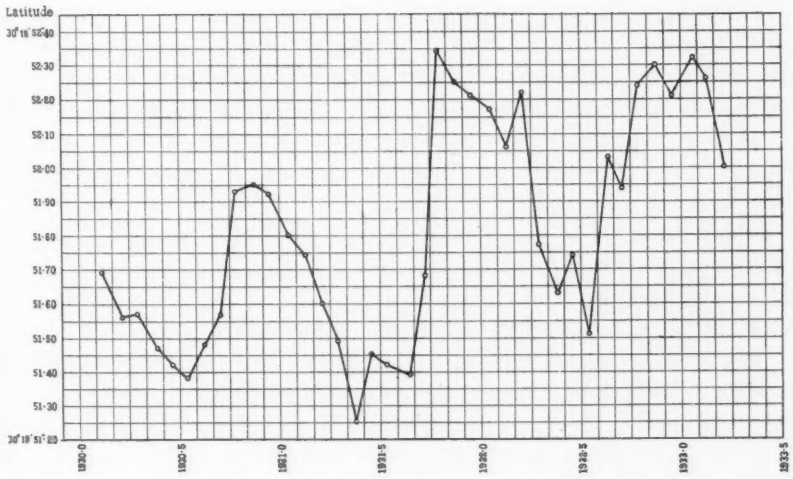



FIG. 1.

Variation of Latitude at Dehra Dūn (1930—33)

free from declination errors and should depict variations of latitude correctly. This has been claimed as the chief advantage of the chain method, namely, that the effect of the errors of declinations of the stars is eliminated.

The variation of latitude at Dehra Dūn deduced by the above method is exhibited graphically in Plate XVII, *Survey of India Geodetic Report*, 1933. On page 119 of *Survey of India Geodetic Report*, 1934, it is mentioned that this curve requires some corrections. Fig. 1 represents the corrected curve.

The above argument about the chain method is however much too simple. Many causes combine to produce the closure error C. If it were due to accidental errors it should be positive or negative at random for different years even if the same programme were used every year. But at Pulkowa and at the stations of the International Latitude Service, it was found to be negative every year. Using mean difference for 3 years (1899–1902), Albrecht[2] found C for each of the six stations of the International Latitude Service to be as follows :—

| | | | |
|---|---|---|---|
| Mizusawa | $= -0''\cdot061$ | Gaithesburg | $= -0''\cdot063$ |
| Tschardgiri | $= -0\cdot440$ | Cinceinnati | $= -0\cdot132$ |
| Carloforte | $= -0\cdot111$ | Ukiah | $= -0\cdot238$ |

Mean C $= -0''\cdot141$.

For the same stations the mean closure error for the years 1900–1905 is $-0''\cdot219$, for the years 1906–11, it is $-0''\cdot224$, and for the years 1912–14, it is $-0''\cdot248$.[3]

C has thus all the appearances of a systematic error. At Dehra Dūn, however we see from Table II, that it changes its sign during the 3 years of observation, although on the whole it keeps a negative sign.

The physical cause which gives rise to the closure error is not yet clear. We will consider some of the important systematic causes, which contribute towards it. Two such causes are the diurnal and annual variation of latitude.

From equation (1), we see that in the formation of the chain, the later observations are always subtracted from the earlier ones. Hence, a diurnal variation of latitude, or any other short period fluctuation would produce a systematic error in each group difference, and a closure error would result.

The existence of this diurnal variation is now well established, although its origin is uncertain. In addition to this diurnal term, there might be other short period terms. On analysing the variation of latitude observations, several tidal components have been detected by different people. As a matter of fact, it is to be recommended at the next meeting of the International Union of Geodesy and Geophysics, that a harmonic analysis should

be made of latitudes observed at the various International latitude observatories in order to detect the principal short period components $M_2$, $S_2$, $K_2$, $N_2$, $K_1$ and $O_1$. The following equations show the relation between the closure error and the diurnal term :—

Let $\phi_0$ denote the true value of latitude at epoch $t_0$.

$p_{e,r}$ the evening observation of $p$th group on the $r$th day.

$(p+1)_{m,r}$ the morning observation of $(p+1)$th group on the $r$th day.

$\phi_{p,e,r}$, $\phi_{p+1,m,r}$ the values of observed latitudes from $p$th and $(p+1)$th groups on the $r$th day.

$t_{p,e,r}$, $t_{p+1,m,r}$ the epochs of observation of $p$th and $(p+1)$th groups.

$\Delta\delta_p$, $\Delta\delta_{p+1}$ the corrections to adopted declinations of the $p$th and $(p+1)$th groups.

$\Delta\mu_p$, $\Delta\mu_{p+1}$ the corrections to adopted proper motions of the $p$th and $(p+1)$th groups.

Z the Kimura term.

$\Delta\phi$ the increase of latitude per unit time.

$a\cos(T-\epsilon)$ the diurnal variation of latitude, T being reckoned from midnight.

Then,

$$\left.\begin{aligned}&\phi_{p,e,r} + \Delta\delta_p + \Delta\mu_p\,(t_{p,e,r} - t_0) - Z_{p,e} - a\cos\,(T_{p,r} - \epsilon)\\ &\quad - \Delta\phi\,(t_{p,e,r} - t_0) = \phi_0\\ &\phi_{p+1,m,r} + \Delta\delta_{p+1} + \Delta\mu_{p+1}\,(t_{p+1,m,r} - t_0) - Z_{p+1,m}\\ &\quad - a\cos\,(T_{p+1,r} - \epsilon) - \Delta\phi\,(t_{p+1,m,r} - t_0) = \phi_0\end{aligned}\right\}\cdots \quad (2)$$

$$\begin{aligned}\phi_{p,e,r} - \phi_{p+1,m,r} &= (\Delta\delta_{p+1} - \Delta\delta_p) + \Delta\mu_{p+1}\,(t_{p+1,m,r} - t_0)\\ &\quad - \Delta\mu_p\,(t_{p,e,r} - t_0) + (Z_{p,e} - Z_{p+1,m})\\ &\quad + a\,\{\cos\,(T_{p,r} - \epsilon) - \cos\,(T_{p+1,r} - \epsilon)\} - \Delta\phi\,(t_{p+1,m,r} - t_{p,e,r}) \cdots \quad (3)\end{aligned}$$

This equation holds for any day $r$ of observations of groups $p$ and $(p+1)$. If this group is observed for $n_p$ days, then summing up for all the days of observation, we have

$$\begin{aligned}\frac{1}{n_p}\sum_{r=1}^{n_p}(\phi_{p,e,r} - \phi_{p+1,m,r}) &= (\Delta\delta_{p+1} - \Delta\delta_p) + \Delta\mu_{p+1}\,(\bar{t}_{p+1,m} - t_0)\\ &\quad - \Delta\mu_p(\bar{t}_{p,e} - t_0) + (\bar{Z}_{p,e} - \bar{Z}_{p+1,m})\\ &\quad + \frac{a}{n_p}\sum_{r=1}^{n}\{\cos\,(T_{p,r} - \epsilon) - \cos\,(T_{p+1,r} - \epsilon)\} - \Delta\phi\,(\bar{t}_{p+1,m} - \bar{t}_{p,e}),\end{aligned}$$

where $\bar{t}_{p+1,m}$, $\bar{t}_{p,e}$ are the mean epochs of observation of the two groups.

$$\begin{aligned}\therefore\ \bar{\phi}_{p,e} - \bar{\phi}_{p+1,m} &= (\Delta\delta_{p+1} - \Delta\delta_p) + (\Delta\mu_{p+1} - \Delta\mu_p)\,(\bar{t}_{p,e} - t_0)\\ &\quad + (\bar{Z}_{p,e} - \bar{Z}_{p+1,m})\\ &\quad + \frac{2a}{n}\sum_{r=1}^{n}\left\{\sin\left(\frac{T_{p+1,r} - T_{p,r}}{2}\right)\sin\left(\frac{T_{p+1,r} + T_{p,r}}{2} - \epsilon\right)\right\}\\ &\quad - \Delta\phi\,(\bar{t}_{p+1,m} - \bar{t}_{p,e}) \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (4)\end{aligned}$$

$\bar{t}_{p+1,m} - \bar{t}_{p,e} \doteqdot 4$ hours, so the last term can be neglected, if we assume that diurnal variation is the only short period variation of latitude.

Also $\bar{Z}_{p+1,m} - \bar{Z}_{p,e}$ can be neglected, as Z is an annual term. We will see later on, that Z is of the form $a \cos(T + \epsilon_1) + b \cos(2T + \epsilon_2) + c \cos(T + \odot + \epsilon_3)$. We will assume the first term to be included in the diurnal term, and the last two terms we will neglect for the present discussion.

Summing up equation (4) from $p = 1$ to $p = 6$, *i.e.*, for all the groups, we get

$$\sum_{p=1}^{6} (\bar{\phi}_{p,e} - \bar{\phi}_{p+1,m}) = \sum_{p=1}^{6} (\Delta\mu_{p+1} - \Delta\mu_p)(\bar{t}_{p,e} - t_0)$$

$$+ \sum_{p=1}^{6} \frac{2a}{n_p} \sum_{r=1}^{n} \sin\left(\frac{T_{p+1,r} - T_{p,r}}{2}\right) \sin\left(\frac{T_{p+1,r} + T_{p,r}}{2} - \epsilon\right) \quad \cdots \quad (5)$$

The first term on the right hand side is

$$\Delta\mu_1 (\bar{t}_{6,e} - \bar{t}_{1,e}) + \Delta\mu_2 (\bar{t}_{1,e} - \bar{t}_{2,e}) + \ldots\ldots + \Delta\mu_6 (\bar{t}_{5,e} - \bar{t}_{6,e})$$

$$\bar{t}_{2,e} - \bar{t}_{1,e} \doteqdot \bar{t}_{3,e} - \bar{t}_{2,e} \doteqdot \ldots\ldots \doteqdot \bar{t}_{6,e} - \bar{t}_{5,e} \doteqdot \tfrac{1}{6} \text{ year},$$

$$\bar{t}_{6,e} - \bar{t}_{1,e} \doteqdot \tfrac{4}{5} \text{ year}.$$

We see therefore that only $\Delta\mu_1$ is important. The remaining $\Delta\mu$'s are multiplied by a small quantity.

If closure error is known for two years, we can theoretically at least, obtain the amplitude and phase of the diurnal term from equation (5). At Dehra Dūn C is available for 3 years, and so one can solve for $a$ and $\epsilon$ by least squares. But in practice, this method cannot give reliable results, because the observations are only spread over about 4 hours of mean time, which is too small a range. At Dehra Dūn C for the three years under consideration is $-0''{\cdot}25$, $-0''{\cdot}11$, and $+0''{\cdot}08$ and the mean times of observation of the same group are practically identical during the three years. It is apparent that a simple harmonic expression for the diurnal term cannot satisfy the above C's. At Dehra, then the diurnal term is not mainly responsible for the closure error. It might be, that the diurnal term is not the same for different years, in which case of course the closure errors for different years can be widely different.

The diurnal term at Pulkowa[4] is $0{\cdot}05 \cos(T - 15^h)$. This was determined by analysing 12 years' observations. These observations were grouped according to mean time hours and the 24 hourly values analysed. Knowing the diurnal term, its effect on C can readily be computed. At Pulkowa, the above expression seems to account for the closure errors obtained during the years 1904–1915 very satisfactorily.

From (5), we see that the group-reductions deduced by the chain method would show secular variations with time on account of the $\Delta\mu$ term. A knowledge of the accurate values of the proper motions is however a desideratum at present, and as mentioned later, for the stars of the International Latitude Service, the variation of latitude observations themselves are used to determine it. If however this term could be neglected, and if $(e-m)$ were constant, and had the same mean value for each 2-monthly period, then the closure error is distributed correctly. The latter condition may be achieved with sufficient accuracy, if the programme is arranged in such a way, that the mean times of observation of $m$ and $e$ are constant for each group-pair. This of course only holds, if there are no other disturbing short period terms.

Closely associated with the diurnal term is the so-called Kimura term which was first announced by Kimura[5] in 1902, as having an annual period, its amplitude being the same at all the stations. Nowadays, it is supposed to be composed of two parts Z′ and Z, the former of which is constant at all stations, while the latter is peculiar to each station and is much the more important.

For the International Latitude stations, Z′ is obtained by forming the equations $x \cos \lambda + y \sin \lambda + Z' = \Delta\phi$ for three stations, and solving them simultaneously. The local part Z of the Kimura term is to a large extent dependent on local meteorological conditions.

An attempt has been made to deduce local Z at Dehra Dūn in two ways :—

(*a*) By the chain method.

(*b*) By consideration of evening and morning observations of the same group.

*Method* (*a*).—The relative errors of declination of the various groups from the 3 years' observations are shown in Table II. Taking the mean values of these for the three years, each group-mean (G.M.) is brought in terms of the first group. We thus get a uniform system of Instantaneous latitudes.

These values are shown in Table III, in which the first column denotes epoch of observation, second column the (Mean-Instantaneous latitude), *i.e.*, variation of latitude at Dehra Dūn. Third column is the variation of latitude computed from the International co-ordinates $x$ and $y$. Fourth column is the difference of the second and third columns and should give the Z-term at Dehra. In the second column, mean differences of $\delta$'s for the three years are used. To a certain extent, it would be better to use actual differences of each year, distributing C of each year separately, because we do not know the cause of this C.

TABLE III.

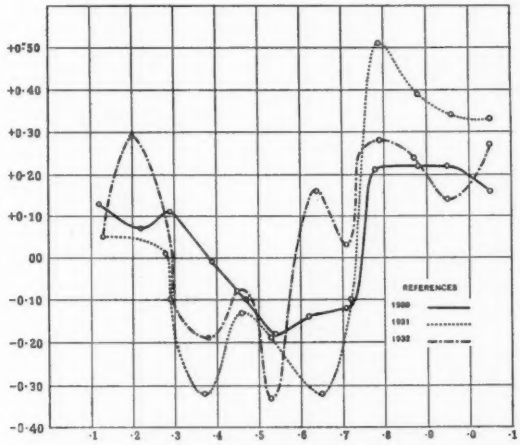
*Z-term at Dehra Dūn.*

| Date | Dehra | International | Dehra-Int. =Z-term | ·185×Sin (2$\theta$–$\alpha$–27°·8) | ·21×Sin ($\theta$–$\alpha$–24°·7) | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|---|
| 1930·12 | +·05 | −·08 | +·13 | +·19 | +·16 | −·06 | −·03 |
| ·22 | −·08 | −·15 | +·07 | +·06 | +·06 | +·01 | +·01 |
| ·29 | −·07 | −·18 | +·11 | +·03 | +·12 | +·08 | −·01 |
| ·39 | −·17 | −·16 | −·01 | −·14 | +·04 | +·13 | −·05 |
| ·47 | −·22 | −·12 | −·10 | −·15 | +·10 | +·05 | −·20 |
| ·54 | −·26 | −·08 | −·18 | −·17 | −·01 | −·01 | −·17 |
| ·62 | −·16 | −·02 | −·14 | −·10 | −·03 | −·04 | −·11 |
| ·71 | −·07 | +·05 | −·12 | −·02 | −·02 | −·10 | −·10 |
| ·78 | +·29 | +·08 | +·21 | +·02 | +·03 | +·19 | +·18 |
| ·88 | +·31 | +·09 | +·22 | +·15 | −·01 | +·07 | +·23 |
| 1930·95 | +·28 | +·06 | +·22 | +·10 | +·14 | +·12 | +·08 |
| 1931·05 | +·16 | +·00 | +·16 | +·18 | +·02 | −·02 | +·14 |

| Date | Dehra | International | Dehra-Int. =Z-term | +·295×Sin (2$\odot$–$\alpha$–5°·3) | +·332×Sin (–$\odot$ $\alpha$–11°·7) | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|---|
| 1931·13 | −·01 | −·06 | +·05 | +·18 | +·06 | −·13 | −·01 |
| ·28 | −·15 | −·16 | +·01 | +·02 | +·03 | −·01 | −·02 |
| ·29 | −·26 | −·16 | −·10 | −·16 | −·01 | +·06 | −·09 |
| ·37 | −·50 | −·18 | −·32 | −·22 | +·08 | −·10 | −·40 |
| ·46 | −·30 | −·17 | −·13 | −·28 | +·11 | +·15 | −·24 |
| ·53 | −·33 | −·14 | −·19 | −·26 | +·06 | +·07 | −·25 |
| ·65 | −·36 | −·04 | −·32 | −·03 | −·10 | −·29 | −·22 |
| ·72 | −·07 | +·03 | −·10 | +·10 | −·10 | −·20 | ·00 |
| ·79 | +·59 | +·08 | +·51 | +·23 | −·13 | +·28 | +·64 |
| ·88 | +·50 | +·11 | +·39 | +·28 | −·08 | +·11 | +·47 |
| ·96 | +·46 | +·12 | +·34 | +·28 | +·10 | +·06 | +·24 |
| 1932·05 | +·42 | +·09 | +·33 | +·23 | −·03 | +·10 | +·36 |

| Date | Dehra | International | Dehra-Int. =Z-term | $+\cdot141\times\sin(2\odot-\alpha-25°\cdot4)$ | $-\cdot048\times\sin(\odot-\alpha-120°\cdot7)$ | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|---|
| 1932·13 | +·06 | +·01 | +·05 | +·14 | −·03 | −·09 | +·08 |
| ·20 | +·22 | −·07 | +·29 | +·06 | −·04 | +·23 | +·33 |
| ·29 | −·23 | −·15 | −·08 | +·00 | −·04 | −·08 | −·04 |
| ·38 | −·37 | −·18 | −·19 | −·09 | −·04 | −·10 | −·15 |
| ·45 | −·26 | −·18 | −·08 | −·11 | −·04 | +·03 | −·04 |
| ·53 | −·49 | −·16 | −·33 | −·14 | −·05 | −·19 | −·28 |
| ·64 | +·03 | −·13 | +·16 | −·11 | −·04 | +·27 | +·20 |
| ·71 | −·06 | −·09 | +·03 | −·01 | −·05 | +·04 | +·08 |
| ·79 | +·24 | −·04 | +·28 | +·02 | −·05 | +·26 | +·33 |
| ·87 | +·30 | +·06 | +·24 | +·11 | −·05 | +·13 | +·29 |
| 1932·95 | +·21 | +·07 | +·14 | +·12 | −·04 | +·02 | +·18 |
| 1933·05 | +·32 | +·05 | +·27 | +·13 | −·05 | +·14 | +·32 |

FIG. 2.
Z-term at Dehra Dūn.




Fractions of the year.

In the course of his attempts to disentangle the $x$ and $y$ components of the motion of the Instantaneous axis from the local Z-term, Kimura discovered that the Z-term can be expressed as

$$\Sigma\, a_n \sin(n\odot - \alpha + A_n) + L \sin(2\odot - 2\alpha + \epsilon_1) + M \sin(2\odot + \epsilon_2),$$

where ⊙ is the longitude of the sun. Of these the first term is of a diurnal as well as annual character and is the most important of the lot. The Z-term for Dehra Dūn is shown graphically in Fig. 2 for the three years. Its range varies considerably from year to year. In 1930, it is 0″·4 ; in 1931, it amounts to 0″·8 ; while in 1932, it is midway between the two. The phase appears to agree broadly for the three years, suggesting that it is due to some systematic physical cause. The figures in column (4) were analysed by the method of least squares for the empirical terms

$$a_2 \sin (2\odot - \alpha + A_2), \text{ and } a_1 \sin (\odot - \alpha + A_1).$$

Columns (5) and (6) show the results of the analysis, and columns (7) and (8) the residuals. These residuals are very large. This was to be expected, as from what has been said above, it is obvious that the quantities in column (4) contain other systematic disturbing elements besides the Z-term. The values of latitude residuals in column (2) are not homogeneous but are burdened with the errors of proper motion of each group, the effect of short period terms, and the incorrect distribution of closure error.

The figures in column (4) are rather striking. The maximum range of Z is 0″·8. For comparison, the table below is copied from *Transactions of the I.A.U.*, Vol. III, 1928. It shows the values of Z at Greenwich deduced from observations made in the years 1919·0 to 1927·0.

| Fraction of year | Z |
|---|---|
| 0·0 | + 0″·006 |
| ·1 | + 0 ·013 |
| ·2 | + 0 ·004 |
| ·3 | − 0 ·012 |
| ·4 | − 0 ·026 |
| ·5 | − 0 ·009 |
| ·6 | + 0 ·015 |
| ·7 | + 0 ·017 |
| ·8 | + 0 ·000 |
| ·9 | − 0 ·012 |

The range here is only 0″·04.

*Method* (*b*).—This method consists in finding the differences of morning and evening observations of the same group. Consider group 1.

$$l_e - l_m = \Delta\mu_1 (t_{1m} - t_{1e}) + (Z_{1e} - Z_{1m}) + \Delta\phi (t_{1e} - t_{1m}) + a [\cos (T_1 - \epsilon) - \cos (T_2 - \epsilon)] \quad \cdots \quad \cdots \quad \cdots \quad (6)$$

$t_{qm} - t_{qe} \doteqdot \frac{1}{6}$ year, except for $q = 1$, when it is about $\frac{4}{5}$ths of a year. So only $\Delta\mu_1$ has a large effect. The remaining $\Delta\mu$'s are multiplied by a small quantity. $\Delta\phi(t_{1e} - t_{1m})$ represents latitude variation in about two months' time, and can be computed by using the International $x$ and $y$. The last term cannot be computed on account of lack of knowledge of diurnal term. Its effect cannot be neglected in general, if the amplitude of the diurnal term is large. This method possesses one chief advantage over the first one, namely, that the error of $\delta$ is cancelled out with certainty. It might be pointed out that in this method, observed $l_e - l_m$ is required. The values of latitude derived from the various groups have not got to be reduced to the first group. Table IV gives the necessary data. The various entries are self-explanatory.

TABLE IV.

*Values of* $(e-m)$.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| Serial No. | Group | Mean Epochs | | Mean Latitude | | Morning observations reduced to epoch of evening | $(v_1)$ $e-m$ | $R_1$ | $R_2$ |
| | | Evening | Morning | Evening | Morning | | | | |
| | | | | 1930—31 | | | | | |
| 1 | I | 1930·18 | 1931·01 | 51·69 | 51·85 | 51·70 | −·01 | +·05 | −·00 |
| 2 | II | 1930·35 | 1930·18 | 51·75 | 51·82 | 51·77 | −·02 | +·03 | +·11 |
| 3 | III | 1930·52 | 1930·35 | 51·72 | 51·86 | 51·94 | −·22 | −·16 | −·10 |
| 4 | IV | 1930·70 | 1930·52 | 51·90 | 51 65 | 51·79 | +·11 | +·20 | +·03 |
| 5 | V | 1930·83 | 1930·70 | 52·13 | 51·83 | 51·87 | +·26 | +·18 | +·11 |
| 6 | VI | 1931·01 | 1930·83 | 51·92 | 52·00 | 51·94 | −·02 | +·04 | −·13 |
| | | | | 1931—32 | | | | | |
| 1 | I | 1931·21 | 1932·01 | 51·59 | 52·25 | 52·02 | −·43 | −·25 | −·02 |
| 2 | II | 1931·35 | 1931·21 | 51·59 | 51·89 | 51·83 | −·24 | −·12 | +·03 |
| 3 | III | 1931·51 | 1931·35 | 51·72 | 51·57 | 51·60 | +·12 | +·26 | +·09 |
| 4 | IV | 1931·70 | 1931·51 | 52·18 | 51·59 | 51·75 | +·43 | +·43 | −·01 |
| 5 | V | 1931·86 | 1931·70 | 52·59 | 52·26 | 52·36 | +·23 | +·32 | +·07 |
| 6 | VI | 1932·01 | 1931·87 | 52·25 | 52·31 | 52·31 | −·06 | −·05 | +·07 |
| | | | | 1932—33 | | | | | |
| 1 | I | 1932·18 | 1933·02 | 52·08 | 52·30 | 52·21 | −·13 | −·05 | +·07 |
| 2 | II | 1932·35 | 1932·18 | 51·99 | 52·37 | 52·25 | −·26 | −·20 | −·08 |
| 3 | III | 1932·50 | 1932·35 | 51·94 | 51·84 | 51·84 | +·10 | +·16 | +·10 |
| 4 | IV | 1932·68 | 1932·50 | 52·19 | 51·88 | 51·94 | +·25 | +·03 | +·02 |
| 5 | V | 1932·85 | 1932·68 | 52·48 | 52·20 | 52·35 | +·13 | −·01 | +·00 |
| 6 | VI | 1933·02 | 1932·85 | 52·36 | 52·40 | 52·40 | −·04 | +·10 | +·04 |

Column (7) is the correction for latitude variation. Neglecting the first term of (6), we have

$$I_e - I_m - \Delta\phi\,(t_{1e} - t_{1m}) = Z_{1e} - Z_{1m} \quad \cdots \quad \cdots \quad \cdots \quad (7)$$

Column (8) gives the L.H.S. of equation (7)

Let $Z = a_2 \sin (2\odot - \alpha - A_2)$,

$Z_e - Z_m = 2a_2 \sin (\odot_e - \odot_m) \cos \{(\odot_e + \odot_m) - (\alpha + A_2)\}$

$\therefore 2a_2 \sin (\odot_e - \odot_m) \cos \{(\odot_e + \odot_m) - (\alpha + A_2)\} = v \quad \ldots \quad (8)$

There are six equations of this type for each year, from which values of $a_2$ and $A_2$ can be deduced by least squares. Again let $Z = a_1 \sin (\odot - \alpha - A_1)$. We then get six observation equations of the form

$$2a_1 \sin\left(\frac{\odot_e - \odot_m}{2}\right) \cos\left(\frac{\odot_e + \odot_m}{2} - \alpha - A_1\right) = v, \text{ for each year.}$$

The figures in column (8) were analysed for the $(\odot - \alpha)$ term. The results are as follows :—

$$\left.\begin{aligned} &1930\text{–}31,\ Z = +0''\cdot09 \sin (\odot - \alpha - 229^\circ) \\ &1931\text{–}32,\ Z = +0''\cdot46 \sin (\odot - \alpha - 108^\circ) \\ &1932\text{–}33,\ Z = +0''\cdot20 \sin (\odot - \alpha - 224^\circ) \end{aligned}\right\} \quad \ldots \quad \ldots \quad (9)$$

$R_1$ shows the residuals after eliminating the Z-term as given by equations (9). These residuals are comparable with the original figures, indicating that the above formulæ for Z are spurious. Now the $(\odot - \alpha)$ term is both annual and diurnal in character. We have thus got a confirmation of our previous results, which we deduced from a consideration of the closure errors, namely, that the diurnal term is not a dominant feature of the Dehra latitude observations.

The observations were next analysed for the $(2\odot - \alpha)$ term with the following results :—

$$\left.\begin{aligned} &1930\text{–}31,\ Z = +0''\cdot09 \sin (2\odot - \alpha - 35^\circ) \\ &1931\text{–}32,\ Z = +0''\cdot24 \sin (2\odot - \alpha - 34^\circ) \\ &1932\text{–}33,\ Z = +0''\cdot13 \sin (2\odot - \alpha - 34^\circ) \end{aligned}\right\} \quad \ldots \quad \ldots \quad (10)$$

Residuals are now given under column $R_2$, and we see that this term must represent the major portion of the Kimura term at Dehra. The year 1931–32 is of special interest, as during this year, $(e - m)$ has an exceptionally large range of $0''\cdot67$. So good is the fit of the empirical term above, that this range is reduced to $0''\cdot11$.

The residuals $R_2$ were further analysed for the $(\odot - \alpha)$ term, but no significant result could be obtained.

Kimura[6] in his report to the International Union of Geodesy and Geophysics at Prague uses a different method for getting the diurnal and Z-term for the International stations, which is only possible, when observations at 3 or more stations using the same star programme are available. He determines a quantity $\Delta\delta'$ from the observations of the same group at the 3 stations by the solution of simultaneous equations, and tabulates the quantity

$\Delta\delta_e' - \Delta\delta_m'$, which is really the same as $Z_e - Z_m$. From an analysis of these quantities he gets

$$Z = -0{\cdot}100'' \cos(\odot - \alpha + 13°) + 0{\cdot}015'' \sin(2\odot - \alpha - 13°) \cdots \quad (11)$$

The amplitude of the first term is assumed arbitrarily. It might be remarked however, that the yearly values in Table IV of the above report, from which the expression for diurnal and Z-terms is deduced by Kimura, are very ragged, and the mean of the 4 years' observations as given in the last column of the table are by no means representative values. The above expression is therefore not very reliable. The reason probably is, that the Z-term depending as it does on the local meteorological conditions varies from year to year, and one cannot deduce it from a number of years' observations. In any case, its recurrence is not certain enough in a place, so badly situated as Dehra Dūn. This is why it has been deduced at Dehra Dūn from each year's observations separately, and not from a combination of the 3 years' results, which otherwise would have been the logical procedure.

There is yet one more systematic term, about which there has been so much misunderstanding, that it needs a special mention. This is the aberration term. It has been mentioned above that the closure errors appear to be always negative and of systematic character. At one time, it was thought that this was due to an error in the constant of aberration used. The aberration term in latitude computations occurs in the reduction of mean places of stars to apparent.

Apparent $\delta$ = mean $\delta$ at the beginning of the year +

$$(Aa' + Bb') + (Cc' + Dd') + t\Delta c'.$$

If $\delta k$ is the correction to the value $k$ of the constant of aberration, then $(Cc' + Dd')$ becomes $Cc' + Dd' + \delta(Cc' + Dd')$.

Now $\phi = \frac{1}{2}(\delta_n + \delta_s) \pm \frac{1}{2}(M_w - M_E)$,

$\therefore$ correction $d\phi$ to latitude is

$$d\phi = d(Cc' + Dd') = -\delta k [\cos \odot \sin \epsilon \cos \phi + \sin \phi \sin(\odot - \alpha)] \cdots \quad (12)$$

In the right hand side of equation (12), we have put $\delta \doteqdot \phi$ in the usual expression for $Cc' + Dd'$.

This equation shows that the correction due to using a wrong $k$ is of a diurnal nature and would therefore produce a closure error.

Closure error due to this is

$$C_k = 2\delta_k \sin\phi \left[\sin\frac{a_2 - a_1}{2}\cos\left(\odot_{1c} - \frac{a_1 + a_2}{2}\right) + \sin\frac{a_3 - a_2}{2}\cos\left(\odot_{2c} - \frac{a_2 + a_3}{2}\right) + \cdots\cdot + \sin\left(\frac{a_1 - a_6}{2}\right)\cos\left(\odot_{6c} - \frac{a_6 + a_1}{2}\right)\cdots \quad \cdots \quad \cdots \quad (13)$$

where $\odot_{1e}$, $\odot_{2e}$, ..... are longitudes of the sun at the mean epoch of evening observations of groups 1, 2, 3, etc.

The earlier writers had envisaged the problem of the closure error in a narrow sense, and had attributed it solely to $\delta k$. Thus, in Band I, *Resultate des Internationalen Breitendienstes*, the group reductions and closing error for the six International observatories are tabulated on page 127. Average C for the six observatories is $-0''\cdot141$. A correction of $\delta k = 0\cdot42$ to the adopted aberration constant would make closing error zero and it was then believed that the correct value for $k$ was $20''\cdot512$ instead of $20''\cdot470$. As more observations became available, further correction to $k$ were deduced in the later volumes of the above publication. At Greenwich, a programme of latitude observations was started in 1911, which was designed primarily for an accurate determination of $k$ and from which latitude variation was deduced as a bye-product. Results are published in two small pamphlets.[7] The adopted value of $k$ is $20''\cdot470$. From the 1911–18 observations, $\delta k$ was found to be $-\cdot028$, and from 1919–27, it was found to be $-0\cdot023$. The final value of $k$ from 1911–27 was deduced to be $20''\cdot445$. Kawaski[8] tried to improve on this value of $k$ by taking the wind effect into account, and obtained a value of $20''\cdot451$.

As a matter of interest, the right hand side of equation (13) was computed for the 1930–31 observations at Dehra Dūn, and it was found that the value of $\delta k$ which would account for the closure error is $0''\cdot09$. This is a smaller correction than the one deduced from Greenwich observations. But it is futile to try to improve on the value of $k$ by this method. In view of the experience gained from the observations of the variation of latitude by the chain method, we can say definitely that the closure error and the difference of evening and morning groups is due to some diurnal term, the origin of which is not clearly understood yet. Until such time as the physical cause of this is discovered, it will not be possible to separate the error due to this term and to the adoption of wrong $k$, because both have the same period.

*Meteorological causes.*—The following meteorological causes have been tried to explain the Kimura Z-term :—

(*a*) *Room-refraction.*—Refraction is computed normally by assuming atmosphere to be stratified in circular layers concentric with the earth. But in the neighbourhood of the instrument, this stratification breaks down because the dome in which the instrument is enclosed is at a uniform temperature. Close to the instrument then, the Isopycnic surfaces follow the shape of this dome. Also near the ground, the temperature is subject to a large daily fluctuation and so the Isopycnics cannot be expected to be parallel to each

other near the ground. The computation of the exact amount of room-refraction is beset with difficulty on account of the inaccurate knowledge of the extent of the disturbed area. If, however, temperature observations at various heights close to the instrument are available, one can estimate the order of magnitude of the room-refraction by making some suitable assumptions.

The usual formula for refraction, assuming strata of equal density to be planes, is $\Omega = (\mu_0 - 1) \tan Z$. If the Isopycnic surfaces are tilted above north towards the zenith by a small angle $\theta$, then for a north star,

$$\Omega = (\mu_0 - 1) \tan (Z + \theta) \cdots \quad \cdots \quad \cdots \quad \cdots \quad (14)$$

Suppose now the Isopycnics are plane surfaces upto a height $h$ above the instrument, and let $\mu = \mu_h$ at this level, and $= \mu_0$ at the level of the telescope. The refraction due to this layer computed in the usual way is

$$\Omega_1 = \frac{\mu_0 - \mu_h}{\mu} \tan Z.$$

If the strata are however irregular, and their slope is not constant, then for a north star, the room-refraction is

$$\Omega_R = \Sigma \frac{\Delta\mu}{\mu} \tan \overline{(Z + \theta)}, \cdots \quad \cdots \quad \cdots \quad \cdots \quad (15)$$

the summation being along the path of the ray.

Equation (15) may be put down approximately as

$$\Omega_R = \frac{\mu_0 - \mu_h}{\mu} \tan \overline{(Z + \theta)} \cdots \quad \cdots \quad \cdots \quad \cdots \quad (16)$$

where $\tan \overline{(Z + \theta)}$ is the mean value of $\tan (Z + \theta)$ along the path of the ray, and cannot in general be computed.

We see therefore that the error in a programme which comprises both N. and S. stars cannot be evaluated exactly, unless the form of the Isopycnics is known close to the instrument. The error however tends to cancel out in the mean, if the Isopycnic surfaces are curved symmetrically about the instrument, which is quite likely if the construction of the observatory is symmetrical.

Larmor[9] has suggested that $(\mu_0 - \mu_h)$ may be different in summer than in winter, giving rise to an annual term in refraction. This fact will not produce any harmful effect if the Isopycnics are flat, or are symmetrically curved, so long as the N. and S. stars are combined in pairs, as is the case in Talcott programme.

(*b*) *Slope of Isopycnic surfaces with a seasonal periodicity.*—Larmor[9] also suggested that if the Isopycnic surfaces are tilted one way during the summer months, and the other way during winter, we would get a convenient

explanation of the Kimura term. Indeed, this explanation has been adopted in *Geodetic Report*, 1933, p. 45. Taking the average amplitude of Z-term at Dehra Dūn to be $0''\cdot3$, it can easily be shown, that this can be explained, if the Isopycnic surfaces were tilted above the N. by about 20 min. of arc in October, November and December, and below the N. by the same amount in June. The slopes of the Isopycnic surfaces are read from the charts published by the Indian Meteorological Department[10], and it is estimated that these layers are tilted upwards towards the N. by about 1 min. in November, and 2 min. in December. A complete quantitative explanation cannot naturally be expected to be derived from such small scale charts, especially as these refer to sea-level, and the actual values of the gradients at Dehra Dūn may be entirely different from that taken from the charts. It is however interesting to see the charts give the right phases but only 1/20th amplitude.

The slope $\theta$ of the Isopycnics can easily be expressed in terms of the horizontal temperature gradients or horizontal pressure gradients.

Let $h_1$, $h_2$ be the heights of two points on an Isopycnic surface, and $(B_1, t_1)$, $(B_2, t_2)$ corresponding values of pressure and temperature at these points. If $a$ is the horizontal distance between these points, then

$$\tan\theta = \frac{h_2 - h_1}{a} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (17)$$

$$h_2 - h_1 = \frac{B_0 t}{g\rho_0} \log_e \frac{B_1}{B_2} = \frac{Rt}{ga} \log_e \frac{T_2}{T_1} \quad \cdots \quad \cdots \quad \cdots \quad (18)$$

If $a$ is reckoned in miles, then $\dfrac{Rt}{g} = 5$ miles,

and
$$\left.\begin{aligned} \tan\theta &= \frac{5}{B}\frac{\partial B}{\partial a} \\ &= \frac{5}{t}\frac{\partial t}{\partial a} \end{aligned}\right\} \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad (19)$$

the gradients being per mile.

Error in refraction produced by the slope $\theta$ is

$$\begin{aligned} d\Omega \operatorname{cosec} 1'' &= (\mu_0 - 1)\,[\tan Z - \tan(Z - \theta)] \\ &= (\mu_0 - 1)\,\theta \operatorname{cosec} 1'' \sec^2 Z \quad \cdots \quad \cdots \quad (20) \end{aligned}$$

From this we see that when $d\Omega \operatorname{cosec} 1'' = 1''$,

$$\theta = \tfrac{1}{6000} \text{ radians} \doteqdot 1^\circ$$

For Dehra Dūn, the tilt required is $\frac{1}{3}^\circ$.

For this tilt, from (19), we see that

$$\frac{\partial B}{\partial a} \doteqdot \frac{1}{900} B \doteqdot 1 \text{ mm. per mile}$$

$$\frac{\partial t}{\partial a} \doteqdot \frac{1}{900} t \doteqdot \tfrac{1}{3}^\circ\text{C. per mile}$$

A barometric gradient of 1 mm. per mile is rather excessive. It is therefore not possible to explain quantitatively the amplitude of the Z-term at Dehra Dūn by the tilt of the Isopycnic surfaces only.

(*c*) *Wind effect.*—This comes practically under the category (*b*). Kawaski[8] on analysing the observations at Mizusawa found a distinct correlation between the direction of the wind, and observed $\phi$. Observations of wind at Mizusawa were started in 1901, and have been carried out continuously since then by self-recording apparatus. He applied his method to Greenwich as well, and found that the part of the latitude variation due to wind effect at Greenwich shows two maxima and two minima during a year. He predicted therefore that the Z-term at Greenwich should contain a variation of semi-annual type, which is actually the case. Dr. H. Spencer Jones[11] has pointed out that the phases of the wind effect, the diurnal term and the Z-term at Greenwich are the same, and that the wind effect is responsible for more than half of the Kimura term at Greenwich.

At Dehra Dūn, unfortunately lack of wind observations makes this research impossible. There are reasons to expect however that very interesting results would have been derived if the requisite data were available. John Eliot's[12] researches show that there is a seasonal and diurnal variation in the direction of the prevailing winds near the Himālayas. The diurnal feature is supposed to be a permanent feature, and the most important winds are due to disturbances of Isopycnic surfaces in a direction perpendicular to the mountains. These disturbances are caused by unequal diurnal heating of the column of air over the plains and mountains, so that the Isopycnic surfaces are lifted by expansion higher over the plains during the day, and are lowered by contraction during the night. Same cause will also give a seasonal variation of the Isopycnic surfaces.

There is no doubt then that meteorological data about the direction and force of the wind, and the Isopycnic surfaces will provide very interesting material for explaining the Z-term.

There is one more factor, which makes wind observations of particular interest at Dehra Dūn, and that is, that there is more chance of the Isopycnic surfaces being flat in strong wind than in calm. In the absence of wind, correlation currents produce irregular distortion in the stratification of air. Now Dehra Dūn is very badly located from this point of view, as it is a markedly calm place, and a large atmospheric effect of this kind would be expected.

Passing from these detailed to more general considerations we see that with the present state of our knowledge, the chain method fails to provide

a harmonious declination system for the investigation of the polar motion. In this method, not only the polar motion, but also $\Delta\mu, \Delta\delta$, Z and the diurnal term have to be treated as unknowns. The ideal programme of observations would be that which would enable these terms to be determined with accuracy.

The methods of determining declination and latitude in astronomy are so intertwined that a change in one cannot be easily distinguished from that in the other. The declination of stars given by observations of meridional circles are not accurate enough, and so we are forced to move in a circle. The method of successive approximations has to be resorted to. In his latest publication, Kimura[13] has reduced the observations at three stations of the International Latitude Service by finding first the $\Delta\delta$'s and $\Delta\mu$'s from the latitude observations themselves assuming a provisional value for latitude variation. The programme is such that the consecutive groups are symmetrically distributed with respect to midnight. This enables the Z-term to be determined with reasonable accuracy and then by equations similar to (4), $\Delta\delta$ and $\delta\mu$ can be solved for. Utilizing these values, the polar motion is solved for finally.

An estimate of the relative magnitudes of $\mu$ and $\Delta\mu$ can be made from the tables on pages 28, 45 and 46 of *Results of the International Latitude Service* from 1922·7 to 1931·0.

For pair $2, \mu = -0{\cdot}013$, and $\Delta\mu = -0{\cdot}010$
,, $6, \mu = -0{\cdot}011$, ,, ,, $= -0{\cdot}016$
,, $13, \mu = -0{\cdot}005$, ,, ,, $= -0{\cdot}028$
,, $40, \mu = -0{\cdot}035$, ,, ,, $= -0{\cdot}053$

The values of the adopted proper motion can thus be in error by over 100%.

Kimura[14] has tabulated the differences between $\delta$'s and $\mu$'s as deduced in Vol. VII of *Results of the International Latitude Service*, and as given in Boss's general catalogue. A scrutiny of the table shows that $\delta_{G.c.} - \delta_{VII}$ for individual pairs may be as much as $0''{\cdot}45$ and $\mu_{G.c.} - \mu_{VII}$ may be as much as $0''{\cdot}169$. The improvement of the declinations and proper motions of the stars is thus a matter of necessity.

The chain method is designed primarily for obtaining the variation of latitude. For geting mean value of latitude it is best to observe a much greater number of star-pairs than those used in the chain method in order to get a result free from errors of $\delta$. Thus at the Lisbon (1933) meeting of the International Union of Geodesy and Geophysics, the Director of the Tokyo Astronomical Observatory reported that for determining the latitude of his observatory, 258 star-pairs were observed for a total period of 455 days. These star-pairs were divided into 31 groups, each group comprising 12 to 16

TABLE V.

*Variation of Latitude with the Interval after New and Full Moon in* 1930.

(*Latitude residuals.*)

| Month | Interval after new moon | | | | | | | Interval after full moon | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2 days | 4 days | 6 days | 8 days | 10 days | 12 days | 14 days | 2 days | 4 days | 6 days | 8 days | 10 days | 12 days | 14 days |
| February .. | 0″·26 | 0″·26 | 0″·34 | 0″·34 | 0″·19 | 0″·53 | 0″·53 | 0″·30 | 0″·39 | 0″·39 | 0″·18 | 0″·18 | 0″·18 | 0″·18 |
| March .. | ·60 | ·60 | ·60 | ·61 | ·61 | ·35 | ·35 | ·39 | ·39 | ·37 | ·47 | ·40 | ·40 | ·32 |
| April .. | ·35 | ·35 | ·33 | ·33 | ·33 | ·36 | ·36 | ·54 | ·37 | ·37 | ·31 | ·31 | ·61 | ·61 |
| May { .. | ·51 | ·60 | ·60 | ·60 | ·60 | ·60 | ·46 | ·46 | ·46 | ·36 | ·49 | ·49 | ·63 | ·63 |
| .. | ·57 | ·62 | ·48 | ·48 | ·48 | ·46 | ·61 | ·46 | ·46 | ·55 | ·63 | ·63 | ·75 | ·75 |
| June .. | ·71 | ·88 | ·94 | ·94 | ·94 | ·52 | ·52 | ·41 | ·41 | ·41 | ·41 | ·61 | ·61 | ·61 |
| July .. | ·61 | ·61 | ·61 | ·61 | ·49 | ·54 | ·59 | ·50 | ·50 | ·50 | ·50 | ·50 | ·50 | ·51 |
| August .. | ·51 | ·51 | ·51 | ·59 | ·59 | ·61 | ·26 | ·26 | ·49 | ·49 | ·59 | ·29 | ·42 | ·42 |
| September .. | ·43 | ·43 | ·22 | ·08 | −·04 | ·07 | ·07 | ·10 | ·10 | ·27 | ·27 | ·06 | ·13 | ·13 |
| October .. | ·05 | ·05 | ·05 | −·07 | −·07 | −·11 | −·11 | ·29 | −·03 | —·03 | ·14 | ·14 | ·11 | ·11 |
| November .. | −·01 | ·19 | ·19 | −·06 | ·17 | ·17 | −·03 | ·21 | ·21 | ·21 | −·01 | ·16 | ·16 | ·01 |
| December .. | ·05 | ·05 | ·05 | | | | | | | | | | | |
| Mean .. | +·39 | +·43 | +·41 | +·40 | +·39 | +·37 | +·33 | +·36 | +·34 | +·35 | +·36 | +·34 | +·41 | +·39 |

pairs, but adjacent groups are quite independent and are not related as in the chain method.

There is one further point that might be mentioned, and that is the relation between latitude and moon's age. A. Gougenheim[15] has discussed the observations of latitude made with the prismatic astrolabe at Algiers during October and November 1926 and found that latitude seemed to have a definite relation with the age of the moon. It showed a maximum practically at the time of the new moon and a little after the time of the full moon. He also saw evidence of a semi-lunar period of 14 days in the curve of the variation of latitude.

G. Bomford in *Nature* of June 8, 1929, drew a similar chart for the Dehra Dūn observations of October and November 1926, and found the same close relation.

The above observations of 1930–33 afford a very suitable material for this investigation. In Table V, the mean value of latitude is tabulated against the interval after full and new moon for the year 1930. The table does not give any evidence of a correlation.

The two months' observations (1926) at Algiers and Dehra Dūn utilized by Gougenheim and Bomford show a range of variation of $2''\cdot8$, which is rather large and cannot be real change. With the zenith telescope, two months' observations of mean of 2 groups hardly show a range of $0''\cdot3$. If each group is taken by itself, the range in the above period may be $0''\cdot8$, but usually it is much less. Bomford by taking the mean for 5 days, reduces the range to $0''\cdot5$, which is of the same order of magnitude as the above, but in view of Table V, the correlation must be regarded as fortuitous.

The variation of latitude with the moon's hour angle and altitude has been studied by Stetson[16] in great detail in various papers. He divided his data into three groups according to the various declinations of the moon to allow for the effect of changing declinations of the moon. His results indicate a lunar diurnal variation in latitude with a range amounting to as much as $0''\cdot07$, depending on the hour angle and declination of the moon.

*Summary.*

The diurnal and Z-terms as deduced from the latitude observations at Dehra Dūn during 1930-33 are discussed. The Z-term has different amplitudes during each year and is explained satisfactorily by an empirical term of the form $a_2 \sin (2\odot - \alpha - A_2)$. Its amplitude is so large, that it cannot be explained quantitatively by seasonal periodicity of the Isopycnic surfaces.

The closure errors of the chain during the three years, and some of the causes which produce them are discussed.

The Dehra Dūn observations show no evidence of a relation between latitude variation and moon's age.

REFERENCES.


1. *Survey of India, Geodetic Report,* Vol. VII (p. 21); Vol. VIII (p. 6); 1934 (p. 44).
2. Th. Albrecht, *Resultate des Internationalen Breitendienstes,* Berlin, 1903, Band I.
3. B. Wanach und H. Mahnkopf, *Ergebnisse des Internationalen Breitendienstes,* von 1912–0 bis 1922. 7.
4. Drozd, *Pulkowa Observatory Circular,* No. 5.
5. Kimura, *Ast. Nach.,* 1902, **158**.
6. Kimura, *Travaux de la Section de Geodesie de l' Union Geod: et Geoph: Internationale,* Prague, 1927.
7. Observations made with the Cookson floating Zenith telescope in the years 1911–18 and 1919–27 at the Royal Observatory, Greenwich.
8. Kawaski, *M. N. R. A. S.,* November 1934; *Jap. Jour. of Geodesy and Geoph.,* 1934–35, **12**; **13,** No. 1, 1935.
9. Larmor, *M. N. R. A. S.,* 1915, **35**.
10. Indian Meteorological Department, *Scientific Notes,* 1930, **8**, No. 19.
11. Spencer Jones, *M. N. R. A. S.,* December 1935, **96**.
12. Indian Meteorological Department, *Scientific Notes,* 1930, **8**, No. 19.
13. Kimura, *Results of the Intern. Lat. Service from 1922.7 to 1931.0,* 1935, **7**.
14. Kimura, *Proc. of Imperial Acad.,* 1935, **11**.
15. Gougenheim, *Comptes Rend. de l' Acad. des Sciences,* July 30, 1928.
16. Stetson, *Nature,* 1933, **131,** 437; 1936, **137**, 933.

# THE DIAMAGNETISM OF SOME METALLIC HALIDES.

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## *1. Introduction.*

Hocart[1] determined the magnetic susceptibility of some polar halides (sodium chloride, potassium chloride and calcium chloride) in the state of solid and in aqueous solutions. More recently Flordal and Frivold[2] have extended these measurements with considerable precision to a large number of salts, mostly halides of the alkali and alkaline earth metals. These observations suggest that the susceptibility of a salt in solution is usually greater than its value in the solid state. The results of Flordal and Frivold show further that the difference in susceptibility is greater for divalent than for univalent salts. In divalent salts the maximum change observed was about 5 per cent. while in a few univalent salts, it was nearly 3 per cent. However, in a number of salts of the latter group, the difference was negligibly small.

It is not clear how much of this change in susceptibility is really due to the different conditions of the ions of the salt in the solid and dissolved states. It is well known that in the case of the halides of the alkali metals the ions are of inert gas configuration and are hence rigid. Applying the rules of Fajans[3] it is evident that their deformation in the solid state should be very small. Hence the change in the susceptibility of the ions in solution should be insignficant. The change observed is generally attributed to the changes in the diamagnetism of water owing to the formation or breaking up of complexes.

In the case of the ionic crystals it is legitimate to regard the additive law of ionic susceptibilities to hold good.[4] But there are many salts which are not truly ionic (or electrovalent) as shown by various lines of evidence: crystal analysis, conductivity, volatility, solubility, etc. The salts of zinc, cadmium and mercury belong to this class of salts.[5] The halides of these elements have much less of the character of salts than those of the alkaline earths. They are covalently linked compounds. The iodides of these salts crystallise in the 'layer lattice' (*schichtengitter*) which is intermediate between the ionic and the molecular lattices. In such salts the additive law of ionic susceptibilities does not hold good.

Krishnamurthi[6] and later Venkateswaran[7] investigated the Raman spectra of some metallic halides. They find that the presence of a covalent

bond is necessary for the production of Raman lines. Thus while the halides of zinc, cadmium and mercury give Raman spectra, the electrovalent halides like magnesium chloride and potassium chloride do not give any displaced lines. The intensity of the lines whenever observed was found to depend on the strength of the covalency bond.

In view of the foregoing considerations, it was felt that it would be of interest to study the diamagnetism of a few halides of zinc, cadmium and mercury in the solid and dissolved states. Large changes in the susceptibility value may be expected in the solutions of these salts.

### 2. *Experiment.*

The investigations were carried out with a Curie balance. The procedure was similar to that adopted in ealier work.[8] Water was taken as the standard substance, its susceptibility at 30° C. being taken as 0·720.* The error in susceptibility measurements may be taken to be less than ½ per cent. The salts used were of the highest purity from Kahlbaum or Merck. The solvents employed in this investigation, namely, water and methyl alcohol, were carefully distilled several times before use.

The following halides were investigated in the solid state and in aqueous solutions : potassium chloride, cadmium chloride, cadmium bromide, cadmium iodide and zinc iodide. Solutions in methyl alcohol of cadmium bromide, cadmium iodide and mercuric chloride were also studied.

### 3. *Results.*

In the following table are shown the values of the diamagnetic susceptibility of the above salts in the solid state. The results of a few other investigators are also shown for comparison.

TABLE I.

| Salt | Values of diamag. susc. | | | |
|---|---|---|---|---|
| | Author | Kido[9] | Flordal and Frivold | Int. Crit. Tables |
| KCl | 0·519 | | 0·516 | 0·516 |
| $CdCl_2$, $H_2O$ | 0·411 | 0·368 | | 0·32 |
| $CdBr_2$, $4H_2O$ | 0·382 | 0·343 | 0·321 | 0·38 |
| $CdI_2$ | 0·297 | 0·308 | | 0·32 |
| $ZnI_2$ | 0·306 | | | |
| $HgCl_2$ | 0·301 | 0·298 | | 0·19 |

The value for methyl alcohol was found to be 0·687.

* All susceptibility values in this paper are given in 10 units.

In the following tables, the results obtained for various solutions are given. The first column gives the concentration of the solution (the number of grams of salt dissolved in 100 g. of the solution). The observed value of the susceptibility of the solution is shown in the second column. The next column gives the susceptibility value calculated on the basis of the additive law. The total change in susceptibility ($\chi_D - \chi_{Solid}$) for 100 g. of the salt when completely dissolved is shown in the last column.

TABLE II.

*Cadmium Chloride in Water.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 27·4 | 0·639 | 0·635 | 0·004 | 0·015 |
| 36·9 | 0·612 | 0·606 | 0·006 | 0·016 |
| 54·6 | 0·560 | 0·551 | 0·009 | 0·016 |
| 63·5 | 0·532 | 0·524 | 0·008 | 0·013 |
| 64·9 | 0·527 | 0·519 | 0·008 | 0·012 |
| 66·0 | 0·524 | 0·516 | 0·008 | 0·012 |
| | | | Average | 0·014 |

TABLE III.

*Cadmium Bromide in Water.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 40·4 | 0·594 | 0·583 | 0·011 | 0·027 |
| 45·0 | 0·580 | 0·568 | 0·012 | 0·027 |
| 69·0 | 0·506 | 0·486 | 0·020 | 0·029 |
| 72·5 | 0·498 | 0·475 | 0·023 | 0·032 |
| | | | Average | 0·029 |

TABLE IV.

*Cadmium Bromide in Methyl Alcohol.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 34·0 | 0·592 | 0·583 | 0·010 | 0·030 |
| 34·2 | 0·593 | 0·582 | 0·011 | 0·032 |
| 46·2 | 0·563 | 0·546 | 0·017 | 0·037 |
| 50·4 | 0·550 | 0·533 | 0·017 | 0·034 |
| | | | Average | 0·033 |

TABLE V.

*Cadmium Iodide in Water.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 34·6 | 0·596 | 0·574 | 0·022 | 0·064 |
| 35·7 | 0·593 | 0·569 | 0·024 | 0·068 |
| 37·9 | 0·582 | 0·559 | 0·023 | 0·061 |
| 38·3 | 0·582 | 0·558 | 0·024 | 0·062 |
| 38·6 | 0·582 | 0·557 | 0·025 | 0·064 |
| 49·1 | 0·548 | 0·512 | 0·036 | 0·073 |
| | | | Average | 0·066 |

TABLE VI.

*Cadmium Iodide in Methyl Alcohol.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 37·5 | 0·567 | 0·542 | 0·025 | 0·066 |
| 38·1 | 0·554 | 0·539 | 0·021 | 0·056 |
| 38·7 | 0·560 | 0·536 | 0·024 | 0·063 |
| 48·0 | 0·533 | 0·500 | 0·033 | 0·067 |
| 61·6 | 0·492 | 0·447 | 0·045 | 0·073 |
| 65·8 | 0·467 | 0·430 | 0·037 | 0·056 |
| | | | Average | 0·064 |

TABLE VII.

*Zinc Iodide in Water.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 51·0 | 0·529 | 0·509 | 0·020 | 0·039 |
| 55·2 | 0·512 | 0·492 | 0·020 | 0·036 |
| 71·4 | 0·443 | 0·425 | 0·018 | 0·025 |
| 72·2 | 0·448 | 0·421 | 0·027 | 0·037 |
| 74·9 | 0·439 | 0·410 | 0·029 | 0·039 |
| 78·4 | 0·417 | 0·396 | 0·021 | 0·027 |
| | | | Average | 0·034 |

TABLE VIII.

*Mercuric Chloride in Methyl Alcohol.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 33·8 | 0·558 | 0·556 | +0·002 | +0·006 |
| 36·4 | 0·545 | 0·546 | −0·001 | −0·003 |
| 43·8 | 0·515 | 0·517 | −0·002 | −0·005 |
| 45·8 | 0·512 | 0·510 | +0·002 | +0·004 |
| 47·1 | 0·504 | 0·505 | −0·001 | −0·002 |
| 55·3 | 0·475 | 0·474 | +0·001 | +0·002 |

TABLE IX.

*Potassium Chloride in Water.*

| Concentration % | $\chi_{Soln.}$ | $\chi_{Add.}$ | $\chi_{Soln.} - \chi_{Add.}$ | $\chi_D - \chi_{Solid}$ |
|---|---|---|---|---|
| 18·8 | 0·682 | 0·682 | 0·000 | 0·000 |
| 20·9 | 0·680 | 0·678 | 0·002 | 0·009 |
| 21·9 | 0·679 | 0·676 | 0·003 | 0·012 |
| 22·3 | 0·675 | 0·675 | 0·000 | 0·000 |
| 27·5 | 0·666 | 0·665 | 0·001 | 0·004 |
| 27·7 | 0·666 | 0·664 | 0·002 | 0·007 |
| | | | Average | 0·005 |

It will be noticed that generally there is an appreciable change of susceptibility on dissolving a halide. In the cases of cadmium iodide and zinc iodide this change appears to be as much as 22% and 11% respectively. The values of the changes in susceptibility are shown in the following table.

TABLE X.

*Aqueous Solutions.*

| Salt | $\chi_{Soild}$ | $\chi_D$ | $\frac{(\chi_D - \chi_{Solid})}{\chi_{Solid}} \times 100$ |
|---|---|---|---|
| KCl | 0·519 | 0·524 | 1·0 |
| $CdCl_2$, $H_2O$ | 0·411 | 0·425 | 3·4 ± 0·5 |
| $CdBr_2$, $4H_2O$ | 0·382 | 0·411 | 7·6 ± 0·8 |
| $CdI_2$ | 0·297 | 0·363 | 22·0 ± 2 |
| $ZnI_2$ | 0·306 | 0·340 | 11·0 ± 2 |
| $ZnCl_2$* | 0·447 | 0·441 | − 1·2 |

TABLE XI.

*Methyl Alcohol Solution.*

| Salt | $\chi_{Solid}$ | $\chi_D$ | $\frac{(\chi_D - \chi_{Solid})}{\chi_{Solid}} \times 100$ |
|---|---|---|---|
| $CdBr_2$, $4H_2O$ | 0·382 | 0·415 | 8·6 ± 0·8 |
| $CdI_2$ | 0·297 | 0·364 | 21·0 ± 2·5 |
| $HgCI_2$ | 0·301 | 0·301 | 0·0 |

A reference to the above tables shows at a glance that the change of susceptibility is about the same in solutions of both the solvents.

*4. Discussion.*

It is seen from the above table that the increase of susceptibility is small in the case of a polar-salt like potassium chloride. With the exception of

* Taken from the measurements of Flordal and Frivold.

mercuric chloride all the other halides investigated show a considerable change on dissolving in water or methyl alcohol. The increase seems to be largest in the case of iodides and least in the case of chlorides.

A salt may be taken to be composed of oppositely charged ions. There is much evidence to show that in a molecule the cation exerts a deformation on the anion.[10] Fajans[3] has shown that the deforming power of a cation is large (*a*) the smaller its size and (*b*) the greater its charge. Also the ions possessing an inert gas configuration produce less deformation than those that do not possess such closed configurations. On the other hand, anions suffer greater deformation when they are large in size and possess more charge. When ions combine to form a molecule a certain amount of deformation necessarily takes place. A direct application of the conclusions of Fajans shows that in the case of the halides of the alkali and alkaline earth elements, such deformation should be very small. In such salts, therefore, no change of susceptibility is to be expected on dissolving and this is just what is observed.

Considering now the halides of zinc, cadmium and mercury it is evident that the cations must have a large deforming power. The ions lack the inert gas configuration, are small in size and are divalent. Also the deformability must be greatest in the case of the iodine ion since it has the largest size among the halogen ions. Such compounds are not truly ionic compounds. The electrovalent link in the case of the alkali and alkaline earth halides passes over into the covalent link in the case of the halides of zinc, cadmium and mercury because of the interpenetration of the electronic orbits of the atoms. The inter-atomic distance in a covalent molecule is less than the sum of the radii of the ions concerned. Thus the effect of deformation may be considered to activate covalency in a molecule. This produces a fluctuation of angular momentum of the electronic orbits and gives rise to an increase in the paramagnetic component in the Van Vleck expression for the susceptibility of the molecule.[11] The net effect is to lower effectively the susceptibility of the molecule.

Kido[9] has determined the specific susceptibilities of a large number of compounds and compared them with the values deduced from an application of the additive law to the ionic susceptibilities. He obtained close agreement between the two values for truly ionic salts like the halides of the alkali elements but much disagreement was noticed in the case of covalent compounds like cadmium chloride and mercuric chloride.

When these compounds are dissolved in strongly polar solvents, the distortion of the ions in the solid state are largely relieved on account presumably of the attraction of the solvent molecules for the ions of the solute molecules. They also ionise to some extent in water as shown by conductivity

mesaurements, the ionisation decreasing from the chloride to the iodide. Cadmium iodide has been shown to ionise in alcoholic sloutions also and the conductivities in solutions of various alcohols have been measured by several investigators.[12] The action, therefore, of solvents like water or methyl alcohol is to ionise or at least loosen the bond between the ions of the molecules. Such release of deformation is largely responsible for the observed increase of susceptibility of the salts on dissolving. The foregoing considerations based on the conclusions of Fajans also help us to understand why the change is greater in the case of the iodides than in the case of chlorides.

A loosening of the bond may also occur when the salts are melted and here we may quote in support the work of Farquharson and Heymann.[13] He studied the susceptibility of the chlorides of cadmium and mercury and found a large increase on melting. It is also known that these halides become fairly good conductors of electricity on fusion.[14]

A part of the change of susceptibility on solution may be due to the formation of 'auto-complexes' in it, especially in the case of cadmium halides. These complexes are polymers with definite links connecting the component molecules and hence may produce appreciable effects on the magnetic susceptibility.

Venkateswaran[7] studied the Raman spectra of zinc and cadmium halides and found that the lines due to them were of medium or faint intensity. In aqueous and alcoholic solutions, the lines were found to broaden slightly and weaken in intensity. This diminution of intensity is obviously due to the loosening of the covalent bond in the molecule of the salt. No evidence however was obtained for the formation of polymers in cadmium compounds. The lines due to these polymers must have shorter shift and because of their low intensities long exposures may be necessary to record them.

The increase of susceptibility in solutions of the halides studied may be attributed to three causes, (*a*) the release of deformation of the electronic systems of the molecule by the polarising action of the solvent to the extent of producing some dissociation, (*b*) the formation of polymers and (*c*) the depolymerisation of the solvent if it happens to contain polymers. Of these the effect due to the first cause is very large while the other two causes produce only small alterations.

The foregoing explanation does not include the case of mercuric chloride. No change of susceptibility is found on dissolving this salt in methyl alcohol. This seems to be due to the greater binding and stability of the mercuric salts which resist the loosening action of the medium. This assumption is strongly

supported by Raman effect data. It is found that the line due to the mercuric chloride is very intense in the solid state and diminishes only slightly in intensity on dissolving in methyl alcohol.

The behaviour of mercury is quite exceptional in other respects also. It forms far more organic compounds than all the other metals taken together. The compounds of mercury break up into ions to an inconsiderable extent in solution. Its compounds are all anhydrous. An idea of the extent of ionisation of mercuric chloride can be had from an examination of the following table collected from the *International Critical Tables*. C gives the concentration measured in milliformula weight in one litre of the solution and $\lambda$ is the equivalent electrical conductivity.

TABLE XII.

| Salt | C | $\lambda \times 10^6$ | Salt | C | $\lambda \times 10^6$ |
|---|---|---|---|---|---|
| Mercuric chloride* | 17·0 | 2·59 | Cadmium iodide* | 2·0 | 91·2 |
| | 75·4 | 1·51 | | 100 | 29·7 |
| | 392 | 1·25 | | 500 | 18·3 |
| Cadmium chloride* | 10 | 82·9 | Zinc iodide† | 60 | 105 |
| | 70 | 55·2 | | | |
| | 500 | 29·6 | | | |
| | | | Calcium chloride* | 100 | 88 |

* Temperature of the solution 18°C.
† Temperature of the solution 25°C.

It is seen from the above table that the ionisation in the cadmium and zinc halides is comparatively larger than in mercuric chloride. The conductivity of mercuric halides in the molten state is also comparatively low. For example, the specific conductivity of zinc chloride at 318° C. is $8 \times 10^{-4}$ ohms while that of mercuric chloride at 277° C. is only $0{\cdot}8 \times 10^{-4}$. Thus we can attribute the constancy of the magnetic susceptibility of mercuric halides on dissolving to the strong binding existing within the molecule.

I take this opportunity of thanking the authorities of the Annamalai University for the award of a studentship which rendered this work possible. My thanks are also due to Dr. S. Ramachandra Rao for his interest and guidance.

*Summary.*

The diamagnetic susceptibilities of a few halides of zinc, cadmium and mercury have been studied in the state of solid and in solutions of water and

methyl alcohol. Solutions of mercuric chloride in methyl alcohol do not show any departure from the additive law while in all the other cases, an increase in susceptibility is obtained in solutions. The increase is largest in the case of iodides and least in the case of chlorides. The order of change is the same in water and methyl alcohol. The results find an explanation from the conclusions of Fajans relating to inter-ionic deformations. The increase in susceptibility in solution is attributed to the release of deformation of the ions of the molecule by the action of the solvent to the extent of ionisation. These considerations find support from the data on electrical conductivity and the Raman effect.

REFERENCES.

1. *Comp. Rend.*, 1929, **188**, 1151.
2. *Ann. der Phys.*, 1935, **23**, 425.
3. Fajans, *Radioelements and Isotopes, etc.*, 1931, pp. 74–91.
4. Stoner, *Magnetism and Matter*, 1934, pp. 268 and 269.
5. Ref. 3; also Sidgwick, *Electronic Theory of Valency*, p. 90.
6. *Ind. Jour. Phys.*, 1930, **5**, 113.
7. *Proc. Ind. Acad. Sci.*, 1935, **1**, 850.
8. *Proc. Ind. Acad. Sci.*, 1936, **3**, 420.
9. *Sci. Rep. Tohoku Imp. Univ.*, 1932, **21**, 149 and 288.
10. *Proc. Ind. Acad. Sci.*, 1935, **2**, 161.
11. *Theory of Electric and Magnetic Susceptibilities*, p. 277.
12. Mellor, *Comprehensive Treatise*, **4**, p. 580.
13. *Faraday Soc. Trans.*, 1935, **31**, 1004.
14. Biltz, *Zeits. Anorg. Chem.*, 1924, **133**, 312. Also Biltz and Klemm, *ibid.*, 1926, **152**, 267.

# THE RAMAN SPECTRA OF SULPHUR AND PHOSPHORUS.

## Part II. Lattice Oscillations.

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### *1. Introduction.*

The phenomenon of wings accompanying the Rayleigh line in light scattering in liquids has been the subject of detailed investigation by several authors[1] in recent years. If this wing is to be considered as purely due to rotation of molecules as in gases, the existing theories predict that its intensity should start from a minimum near the exciting line and increase to a maximum and then fall off gradually. Experimentally, however, it has been observed that the intensity is a maximum at the Rayleigh line and extends on either side far more than is to be expected purely due to rotation of molecules. This discrepancy has been explained by Bhagavantam[2] who has postulated that some highly anisotropic quasi-crystalline groups of molecules exist in liquids and the 'hindered rotation' of molecules in these groups gives rise to a continuous Raman band whose superposition on the genuine rotational scattering is responsible for the observed effects.

A direct experimental proof for the above postulate of Bhagavantam was furnished by the recent discovery of Gross and Vuks[3] who established by beautiful photographs that the continuous wing observed in benzene, diphenyl ether, *para*-dibromobenzene and naphthalene breaks up into discrete intense lines when these substances are examined in the state of single crystals. They have attributed these new lines to the characteristic oscillations of the crystal lattice. According to them the wing accompanying the

[1] Weiler, *Z. f. Phys.*, 1931, **68**, 782; Rousset, J., *Jour. de Phys. et la Rad.*, 1932, **3**, 555; Trumpy, B., *Kgl. N.V.S.*, 1932, **5**, 16, 18 and 47; Bhagavantam, S., *Ind. Jour. Phys.*, 1933, **8**, 197; Veerabhadra Rao, A., *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 274; Gross, E., and Vuks, M., *Jour. de Phys. et la Rad.*, 1934, **67**, 130; Sirkar, S. C., *Ind. Jour. Phys.*, 1936, **10**, 75.

[2] Bhagavantam, S., *Ind. Jour. Phys.*, 1933, **8**, 197.

[3] Gross, E., and Vuks, M., *Nature*, 1935, **135**, 100, 431 and 998; *Jour. de Phys. et la Rad.*, 1936, **7**, 113.

Rayleigh line in the liquids is only due to the broadening of these new rays and not due to any rotational Raman effect in liquids.

While agreeing with the latter authors as to the existence of quasi-crystalline groups in liquids, Bhagavantam[4] has, however, emphasised that the new lines observed in the organic crystals as well as the wings in the liquid state are present prominently only in optically anisotropic media and owe their origin to the hindered rotation of molecules in the crystals as contemplated by Pauling[5] and not to the vibrations of the crystal lattice.

An entirely different interpretation of the results of Gross and Vuks has been put forward by Sirkar[6] who has investigated this problem specially with a view to determine the true nature of the oscillations giving rise to these lines in crystals. He finds that these lines persist in some cases in solution and their relative intensities and frequency shifts change also with temperature. He concludes therefrom, that they are caused by intermolecular oscillations in polymerised groups of molecules and do not furnish evidence for the persistence of quasi-crystalline groups in liquids. He believes that the wing observed in liquids is an entirely independent phenomenon arising from the rotation of molecules in them.

The subject is thus, of great interest for the proper understanding of the liquid state. The present paper gives a discussion of the results obtained with sulphur and phosphorus in the region of the unmodified line.

## 2. *Experimental.*

In order to investigate the region under consideration, it is important to avoid as much as possible all parasitic light and stray reflections from the face of the crystals. This condition was secured in the present investigation by using carefully distilled liquids of sulphur and phosphorus as described in the first part. Phosphorus was allowed to solidify to a uniform mass and reflection was further minimised by carefully screening about half an inch of the substance near the observation end of the tube from the incident light. Pure crystals of rhombic sulphur formed by slow evaporation from a filtered solution in carbon disulphide were used. Monoclinic crystals were prepared by allowing molten sulphur to cool slowly to 110° C. and maintaining it at that temperature throughout the exposure. The rest of the experimental arrangement was the same as before. Though it would be of great interest to examine the behaviour of the wings at higher temperatures, the darkening of the colour in sulphur and the rapid conversion of

[4] Bhagavantam, S., *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 63.
[5] Pauling, L., *Phys. Rev.*, 1930, **36**, 430.
[6] Sirkar, S. C., *Ind. Jour. Phys.*, 1936, **10**, 109 and 189.

yellow phosphorus to red at higher temperatures prevented a proper investigation to be satisfactorily carried out.

*3. Results and Discussion.*

(*a*) *Sulphur.*—The sharp and fairly intense Raman line observed at 88 cm.$^{-1}$ both as Stokes and anti-Stokes in the rhombic sulphur appears weakly in the monoclinic crystals at 110° C., but slightly displaced to 80 cm.$^{-1}$ This line becomes weak and diffuse in the liquid and has a frequency shift of 80 cm.$^{-1}$ and is completely depolarised. As mentioned in the earlier communications, the other lines of rhombic sulphur appear without any change in frequency, intensity or sharpness in the other states also. In the solution in carbon disulphide the line at 88 cm.$^{-1}$ is masked by the broad wing of the solvent and could not, therefore, be observed. From its non-appearance in the solution in carbon disulphide Krishnamurti[7] concluded that it belongs to the symmetrical oscillations of the $S_{16}$ group. Liquid sulphur[8] contains only $S_8$ molecules and the fact that it appears in it as a depolarised band precludes its assignment to the inter-molecular oscillations of polymerised groups of $S_{16}$ molecule. Since it undergoes changes in frequency, intensity and sharpness in passing to the liquid state, it is highly improbable that it could belong to the inner vibrations of the molecule. It is thus, to be concluded that the line at 88 cm.$^{-1}$ is to be attributed to the degenerate vibrations of the crystal lattice which persists also in the liquid. According to Lindemann[9] sulphur has a lattice frequency of $3 \times 10^{12}$ vibrations per second which in wave-numbers gives 100 cm.$^{-1}$ His formula connecting the melting point and the lattice frequency is strictly applicable only to cubic lattices and the difference between the calculated and the observed values is evidently due to a difference in crystal structure. If we bear in mind that the density of the monoclinic and the liquid sulphur at 115° C. is less than that of rhombic at room temperature, the observed changes in frequency due to variations in density are in a direction which could be expected from the expression given by the latter author. But to calculate the coefficients of expansion of the crystal from the observed changes in frequency with temperature on the assumption that the formula holds good to a first approximation to crystal lattices other than the cubic as has been done by Sirkar[10] for naphthalene, is without justification and any conclusion regarding the nature of such oscillations based upon such calculations has but little significance.

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[7] Krishnamurti, P., *Ind. Jour. Phys.*, 1930, **5**, 105.
[8] Ephraim, *Anorganische Chemie*, Steinkopff, Dresden and Leipzig, 1934.
[9] Lindemann, F. A., *Phys. Zeit.*, 1910, **11**, 609.
[10] Sirkar, S. C., *Ind. Jour. Phys.*, 1936, **10**, 114.

(*b*) *Phosphorus.*—Besides the three vibration frequencies, the Rayleigh line in liquid phosphorus is accompanied on either side by a completely depolarised wing. Its intensity starts from a maximum at 5461 A.U. and ends rather abruptly at a distance of about 70 cm.$^{-1}$ on either side. Under very careful conditions of experimentation it is observed that the wing is replaced in the solids by a fairly sharp intense line displaced from the exciting line by 36 wave-numbers. As may be seen from the accompanying plate the anti-Stokes line is more clearly separated than the Stokes from the exciting line.

In the earlier part, it has been pointed out that the Raman effect and the electron diffraction measurements indicate that phosphorus molecule $P_4$ posesses a perfectly tetrahedral structure. In spite of the fact that such a molecule is *optically isotropic*, it is surprising that a completely depolarised wing should accompany the Rayleigh line. The author has also measured the depolarisation of light scattering* in dust-free liquid phosphorus and obtained a value of about 10% which is unexpectedly high for optically symmetrical molecules. A similar observation has been made by previous workers for carbon tetrachloride. These two facts, namely, the occurrence of the wing in Raman scattering and the finite value of depolarisation in Rayleigh scattering in liquid phosphorus, have presumably the same origin as the sharp line at 36 cm.$^{-1}$ in the solid. The existence of a polymer higher than $P_4$ is not known for phosphorus and hence the alternative suggestion that this line may belong to intermolecular oscillations of polymerised groups is out of question.

Since phosphorus crystallises in the cubic system, we can with justification apply the modified formula of Lindemann[11] for the calculation of the frequency of vibration of the crystal lattice. The formula gives $\omega = C\ R^{1/2}\ N^{1/3} \sqrt{\frac{Tm}{MV^{\frac{2}{3}}}}$ where for cubic crystals $C = 2 \cdot 75$, $R^{1/2}N^{1/3} = 0 \cdot 77 \times 10^{12}$ units, $T_m$ the melting point, M is the molecular weight and V is the molecular volume. Taking into consideration the fact that the lattice consists of $P_4$ molecules we have $T_m = 317$, $M = 124$ and $V = 70 \cdot 66$ and get $\omega = 8 \cdot 2 \times 10^{11}$ vibrations per second or $\Delta \nu = 27 \cdot 3$ cm.$^{-1}$ The fairly good agreement between the calculated value and the observed shift is not fortuitous and clearly indicates that this low frequency owes its origin to the degenerate vibrations of the crystal lattice. The crystals persist in the liquid and the broadening of the line gives rise to the depolarised wing.

* The author's thanks are due to Mr. R. S. Krishnan for kindly permitting the use of his experimental outfit for this work.

[11] Lindemann, F. A., *loc. cit.*; see also Gruneisen, E., *Ann. der Phys.*, 1912, **39**, 257.

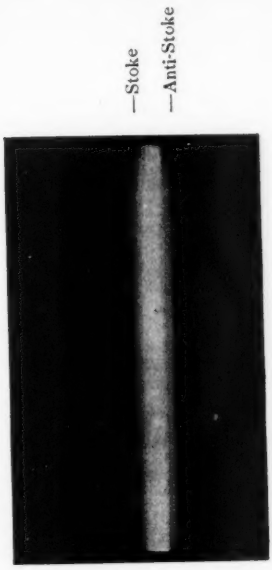
The above results with sulphur and particularly phosphorus suggest that the low frequency lines that have been observed by Gross and Vuks and recently by Sirkar[12] have their origin in the vibrations of the crystal lattice. While the previous observations by the latter authors were restricted mostly to organic molecules whose structures are far from being simple, the well-known crystal structure and state of molecular aggregation of phosphorus exclude the possibility of interpreting the lines as due to hindered rotation of solid molecules or intermolecular oscillations of higher polymers. But in view of the fact that the wing in the liquids like benzene also appears in the vapour state, the latter could not be explained as mainly due to lattice vibrations ; but the superposition of the rotational Raman scattering on the spread-out lines due to the crystal lattice in liquids is responsible for the observed distribution of intensity in the wings. It is also possible that in the case of some substances, Raman lines due either to hindered rotation or to polymerisation or both as well as due to the inner vibrations of molecules may fall in the neighbourhood of the Rayleigh line and every such line has to be examined carefully before any assignment could be made.

In conclusion, it is my desire to thank Sir C. V. Raman for his keen interest in the work.

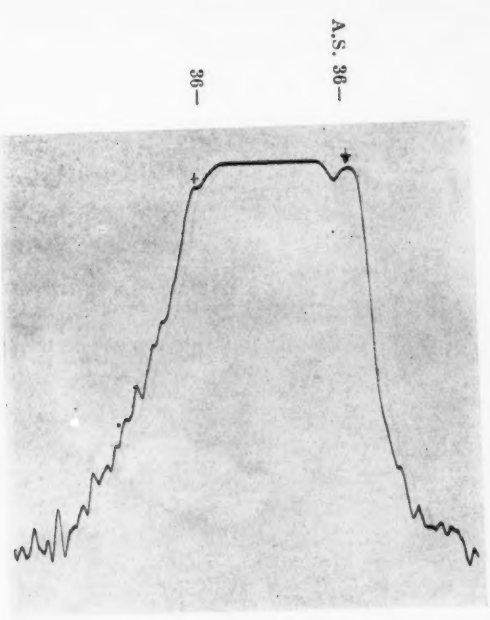
*Summary.*

The existing theories regarding the origin of the discrete Raman lines in the solids in the place of the wings accompanying the Rayleigh line in liquids are reviewed. An intense sharp line at 36 cm.$^{-1}$ has been reported for solid phosphorus which broadens to a depolarised wing in the liquid state. This frequency agrees well with the frequency of vibration of the crystal lattice calculated from the melting point of phosphorus and therefore, owes its origin to the latter. The Raman line at 88 cm.$^{-1}$ observed for rhombic sulphur appears as a weak diffuse depolarised line in liquid sulphur at 80 cm.$^{-1}$ and is also attributed to lattice vibrations. The objections for assigning these lines either to Pauling rotation or to intermolecular oscillations of polymerised groups are indicated.

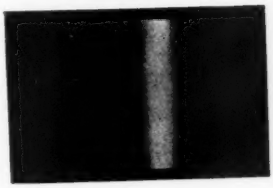
[12] Sirkar, S. C., *Ind. Jour. Phys.*, 1936, **10**, 189.



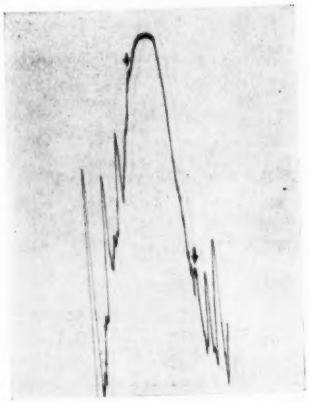

$P_4$ (Solid)



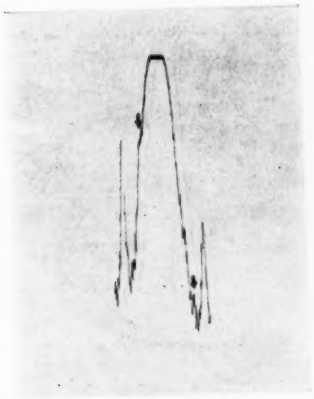

Microphotometric Curve of Solid Phosphorus.



$P_4$ (Liquid) wing




Rhombic Sulphur.




Liquid Sulphur.

**Lattice Oscillations.**

# THE MAGNETIC ANISOTROPY OF RHOMBIC SULPHUR.

By P. Nilakantan.
(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

Received September 30, 1936.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## 1. *Introduction.*

The structure of rhombic sulphur has been recently investigated by B. E. Warren and J. T. Burwell[1] by the method of X-Ray analysis. They found that their results could be satisfactorily interpreted by assuming a symmetrical puckered ring-shaped molecule, consisting of 8 atoms, with a bond angle of 105° and an S–S distance of 2·12 Å. From intensity considerations they deduced the orientation of the molecule in the crystal, and found that the plane of the ring is parallel to the *c* crystallographic axis and makes an angle of about 50° with the *a*-axis.

The magnetic anisotropy of rhombic sulphur has been studied by K. S. Krishnan and his collaborators.[2] At the time of their investigation, however, the necessary data concerning the molecular structure and arrangement were not available for any interpretation of the results to be possible.[3] But in the light of the recently proposed model, the magne-crystallic data assume considerable importance. We can test the general validity of the X-ray analysis by examining whether the results obtained from the magnetic experiments fit in with the suggested scheme of molecular arrangement and structure. And if so, we should also be in a position to get valuable information regarding the magnetic properties of the $S_8$ molecule.

A careful determination of the magnetic anisotropy of rhombic sulphur has been made with the above object in view, and the results are presented in this paper.

## 2. *Experimental.*

The magnetic anisotropy of the crystal was determined by the torsional method developed by Krishnan.[4] The details of experimental arrangement and procedure have been given in an earlier paper by the author.[5] Since the crystal system is orthorhombic, the orientation in the field could be conveniently observed by noting the setting of the crystal edges.

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[1] B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, 1935, **8**, 6.
[2] K. S. Krishnan, B. C. Guha and S. Banerjee, *Phil. Trans.*, 1933, **231**, 235.
[3] For chemical evidence, see Ephraim, *Anorganische Chemie*, Dresden and Leipzig, 1934.
[4] K. S. Krishnan and S. Banerjee, *Phil. Trans.*, 1935, **234**, 267.
[5] P. Nilakantan, *Proc. Ind. Acad. Sci.*, 1935, **2A**, 622.

The direct determination of the torsional constant of the fibre by the oscillating disc method was found to be unsatisfactory in the case of the fine fibres that were used. The modulus of torsion was therefore indirectly evaluated from experiments on a single crystal of calcite suspended with the trigonal axis horizontal, the anisotropy of which in the plane concerned being known with some accuracy.

Special care was taken to prepare sulphur crystals free from impurities. A saturated solution of recrystallised sulphur in Kahlbaum's pure carbon disulphide was allowed to evaporate slowly inside a large bell-jar. Beautiful crystals with well-developed (111) faces were obtained. Experiments were pérformed on six different crystals.

*3. Results.*

The results are shown in Table I below. The mean values of the specific anisotropy, as well as the gram molecular anisotropy for the $S_8$ molecule

TABLE I.

| Mode of suspension | Orientation | Specific Anisotropy $\times 10^8$ | Gram molecular Anisotropy ($S_8$) $\times 10^6$ |
|---|---|---|---|
| *a*-axis vertical | *c*-axis along the field | $\chi_c - \chi_b = 0{\cdot}31$ | $\chi_{c_M} - \chi_{b_M} = 0{\cdot}79$ |
| *b* ,, ,, | *c* ,, ,, | $\chi_c - \chi_a = 2{\cdot}56$ | $\chi_{c_M} - \chi_{a_M} = 6{\cdot}57$ |
| *c* ,, ,, | *b* ,, ,, | $\chi_b - \chi_a = 2{\cdot}27$ | $\chi_{b_M} - \chi_{a_M} = 5{\cdot}82$ |

are given. The usual notation has been adopted $\chi_a$, $\chi_b$, $\chi_c$ standing for the specific susceptibilities along the respective axes. The susceptibilities along the different axes have been computed from a knowledge of the mean susceptibility of rhombic sulphur with the help of the anisotropy data. The calculated values are presented in Table II.

TABLE II.

| Specific susceptibility $-\chi \times 10^8$ | Gram molecular susceptibility ($S_8$) $-\chi_M \times 10^6$ |
|---|---|
| $\chi_a = 0{\cdot}500$ | $\chi_{a_M} = 128{\cdot}2$ |
| $\chi_b = 0{\cdot}478$ | $\chi_{b_M} = 122{\cdot}4$ |
| $\chi_c = 0{\cdot}474$ | $\chi_{c_M} = 121{\cdot}6$ |

Mean susceptibility of rhombic sulphur $\chi = -0{\cdot}484 \times 10^{-6}$.[6]

[6] R. N. Mathur and M. B. Nevgi, *Zeit. Phys.*, 1936, **9–10**, 617.

### 4. *Discussion.*

The results obtained are found to disagree with those of Krishnan. According to him, $\chi_b - \chi_c = 0{\cdot}22$, $\chi_c - \chi_a = 0{\cdot}78$ and $\chi_b - \chi_a = 0{\cdot}94$ (unit $10^{-8}$) which gives $\chi_a > \chi_c > \chi_b$ numerically.[7] But actually we find that $\chi_a > \chi_b > \chi_c$.

In view of the symmetry possessed by the molecule the molecular magnetic constants are evidently the susceptibility in the plane of the ring and that in a direction perpendicular to it. We can also reasonably presume that in such a ring-shaped molecule the diamagnetic susceptibility perpendicular to the plane, should be greater than that in the plane. Then the *c*-crystallographic axis will be the direction of least diamagnetic susceptibility, since, according to X-ray analysis the plane of the ring contains the *c*-axis. Besides, the normal to the plane is given to be nearer to the *a*-axis than the *b*-axis and, therefore, we should have the maximum diamagnetic susceptibility along the *a*-axis. These conclusions are all verified by experiment. Thus it is seen that the general scheme of molecular arrangement suggested by X-ray analysis finds support in the magne-crystallic data. The angle which the plane of the ring makes with the *a*-axis, however, can be independently evaluated from the following relations :

$$\begin{aligned} K_1 &= \chi_{cM} \\ K_1 \cos^2\theta + K_2 \sin^2\theta &= \chi_{bM} \\ K_1 \sin^2\theta + K_2 \cos^2\theta &= \chi_{aM} \end{aligned}$$

Where $K_1$ and $K_2$ are the magnetic moments induced in the molecule along and perpendicular to the plane, respectively, by unit field, referred to a gram-molecule ($S_8$).

$\theta$ = the angle which the normal to the plane makes with the *a*-axis. On calculation we find,

$$\begin{aligned} K_1 &= -121{\cdot}6 \times 10^{-6}, \\ K_2 &= -129{\cdot}0 \times 10^{-6}, \\ \theta &= 19^\circ \text{ nearly.} \end{aligned}$$

It is seen that the plane of the ring makes an angle of 70° nearly with the *a*-axis instead of 50° as given by X-ray analysis.

The feeble anisotropy of the sulphur molecule as compared with that of say, graphite or naphthalene, is no doubt, partly, due to the puckered shape which gives the molecule considerable thickness (1·15 Å). The effective projected mean square radius for the electron charge distribution is only

[7] The actual values given in their paper are 0.07, 0.25 and 0.30 (unit $10^{-6}$) referred to a gram atom (?). The specific anisotropy has been calculated therefrom.

slightly greater in the plane than at right angles to it. In fact, the feebleness of the anisotropy lends support to the idea of a puckered ring.

In conclusion, I wish to express my thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for his encouragement in the course of the work, and valuable criticism.

*Summary.*

The magnetic anisotropy of rhombic sulphur has been determined. The magne-crystallic data are in general agreement with the results of X-ray analysis and support the idea of a puckered ring-shaped molecule consisting of 8 atoms, orientated with the plane parallel to the *c*-axis of the crystal. The magnetic data, however, give the inclination of the plane of the ring to the *a*-axis to be about 70° instead of 50° as suggested by X-ray analysis.

# THE CONVECTION AND VARIATION OF TEMPERATURE NEAR A HOT SURFACE.

## Part I. The Dust-Free or Dark Layer in Relation to Surface Convection.

By M. K. Paranjpe, B.Sc.

(*From the Meteorological Office, Poona.*)

Received September 7, 1936.

(Communicated by Dr. L. A. Ramdas, M.A., Ph.D.)

### 1. *Introduction.*

Tyndall[1] reported in 1870 that in the convection currents rising from a hot body a dark or dust-free region becomes visible when the space near the hot body is illuminated suitably by a strong beam of light. Later, this phenomenon was investigated by a number of other workers.[2,3,4,5] The investigations of Aitken and Lodge and Clark about 1884 brought out the important fact that after accounting for the secondary dust-clearing effects which are produced by (1) the action of heat on clouds of volatile substances, (2) the vertical settling of dust as differentiated from horizontal movements due to convection in the neighbourhood of hot or cold bodies, and (3) the possible centrifugal action associated with the convection round the edges of hot bodies, there still remains the major effect due to the repulsion experienced by dust particles in the neighbourhood of a hot surface (or the attraction experienced by them when they approach a surface which is colder than the air). Aitken and Lodge and Clark showed that, owing to this repelling effect, there is a film of dark or dust-free air surrounding a hot body when it is kept in a dusty atmosphere, and that this film is the source from which the dark ascending cone of hot air above the body draws its supply. The above workers used hot objects of small dimensions in their experiments. Ramdas and Malurkar[6] showed from their experiments with hot plates of large dimensions that the convective heat transfer to the air above the plate is associated with the rising cones of dust-free air which escape from the primary skin layer not at one place but at a number of places and move about in a random manner. Below the extensive hot plate Ramdas and Malurkar found that the dark layer remains more or less uniform.

The convection and distribution of temperature below a hot surface are of great importance in all investigations where the heat transfer across

a gas is under consideration. The present writer undertook a further investigation of this problem at the suggestion of Dr. L. A. Ramdas. The convection below the hot plate and the dark or dust-free layer were studied by the optical method using a dusty atmosphere and a beam of light; the distribution of temperature below the surface was investigated by an interferometric method.

In the present paper we shall confine our attention to certain experiments on the dark layer below a hot surface, for this case is simple to consider. These experiments have led to some new results in the light of which the explanations offered by Aitken and Lodge and Clark would require revision. We shall deal generally with particles in the smoky air which are neither volatile nor hygroscopic.

## 2. *Summary of Previous Work on the Thickness of the Dark or Dust-Free Layer.*

Before entering into a discussion of our results it will be necessary briefly to summarise the main results of previous workers on the dark layer. We reproduce here (Fig. 1) the usual diagram showing the nature of the

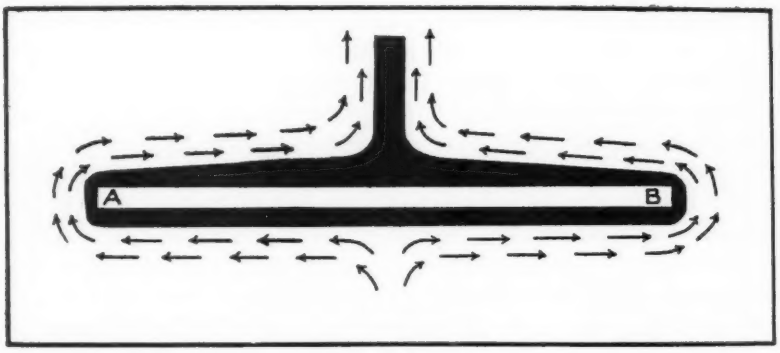


FIG. 1.

convection and the distribution of the dark space when a hot metal plate, say 2 or 3 cm. square, is kept horizontally in an observation chamber containing dusty air. A B is a vertical section of the hot plate and the dark layer which appears under illumination is uniform in thickness below the plate whereas above the plate there is a dark pillar of rising hot air at the centre. Both above and below the plate the outer boundary of the dark layer is sharp. The arrows in the figure indicate the nature of the convectional movements under these circumstances. The air layers below undergo a slight sidewise flow, turn round the edges and then, drifting slightly

towards the centre of the plate, rise upwards. As long as the plate A B is warmer than the air surrounding it, the movements shown in Fig. 1 persist.

(*a*) *Effect of temperature.*—The effect of increasing the temperature of the hot plate has been shown by Lodge and Clark to be to increase the activity of the convective movements in the air. The increase of temperature facilitates the formation of the dark layer more than the increased velocity of the convection currents reduces its thickness. The increase in the thickness of the dark layer with increase of temperature is not, therefore, very conspicuous.

(*b*) *The effect of pressure.*—Lodge and Clark have measured the thickness of the dark layer at different pressures of the surrounding air. The table below is reproduced from their paper.

TABLE I.

| Pressure of air in centimetres of Hg. | Thickness of layer in centimetres |
|---|---|
| 75·9 | ·013 |
| 20·8 | ·027 |
| 10·9 | ·054 |
| 3·9 | ·083 |

The reduction of the pressure in the ratio of 1 : 20 has caused a reduction of the thickness in the ratio of 1 : 6.

(*c*) *Effect in different gases.*—Lodge and Clark estimated the thickness of the dark layer when the hot surface was kept in different gases. Their results are given below :—

| | Thickness of coat in cm. |
|---|---|
| Hydrogen .. .. .. | ·033 |
| Ammonia .. .. .. | ·013 |
| Air .. .. .. .. | ·020 |
| Carbonic acid gas .. .. .. | ·011 |

While the temperature conditions do not appear to have been kept strictly comparable in the experiments with the different gases it is easy to infer that in a light gas like hydrogen the thickness is roughly three times that in the case of carbonic acid gas.

(*d*) *Effect of convection.*—By forcing a current of air against a hot surface one can thin out the dark space and make it ultimately disappear. In otherwise still air, however, the effect of the natural convection which is set up as soon as the hot plate is introduced is to make the dark space slightly thinner below than above ; above the centre of the hot plate the air which

is being made dust-free all round the plate accumulates and rises up vertically as seen in Fig. 1.

A consideration of the above results leads one to the conclusion that we have to reckon with two factors which work in opposition so far as the conditions below the hot plate are concerned. One of them is the repelling force experienced by a dust particle when it goes very close to a hot surface. The repulsion of the particles approaching the surface is opposed by the forces set into operation by the convection pattern below the dark layer.

We shall now describe some experiments made at Poona by the present writer in order to elucidate the problem further.

*3. The Dark Layer between Two Horizontal Plates.*

The convective movements above and below a hot plate make the interpretation of results somewhat difficult. From Fig. 1 one can see that the movements above the plate cause a continuous leakage of the dust-free air formed all round the plate and variations due to temperature and nature of the gaseous medium do not offer results which are sufficiently striking or conclusive. We have accordingly modified the experiments as below:

A vertical section of the apparatus used is shown in Fig. 2. A B C D is a rectangular vessel made of tin. The cross-section is about 5 cm. by 5 cm.

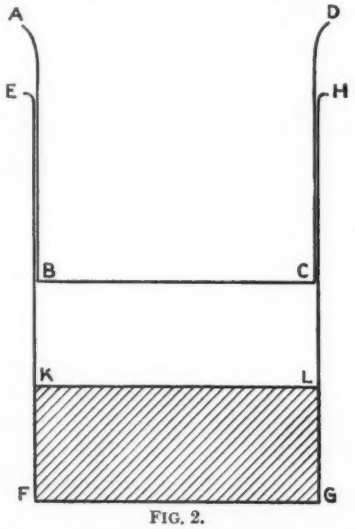


FIG. 2.

This vessel fits exactly into a glass cell E F G H. The lower surface of B C is ground flat. Mercury is poured into the glass cell up to any desired level K L. The metal surface B C is heated by pouring hot water into the vessel

A B C D. To study the phenomena in the interspace, cigarette smoke is introduced into the space between B C and K L, and a parallel beam of light allowed to enter at B K and to get out at C L. The beam is passed through a narrow slit placed vertically outside at the centre of the face B K so that one sees a vertical cross-section of the phenomena taking place between B C and K L. The distance between B C and K L was 2·29 cm., 0·85 cm., 0·54 cm., 0·34 cm. and 0·22 cm. respectively in the different experiments. The results in the different cases are described below. In the experiments referred to below the upper hot surface was always maintained at 75° C. and the cold surface at room temperature.

*Case* 1: *Separation between the surfaces* = 2·29 *cm.*—The vertical section of the convection pattern is shown in Plate XI, Fig. 1. There is a thin dark layer just below the hot plate. The space below this dark layer is occupied by a pair of vortices. The direction and movement of the two vortices is as shown in Fig. 3. The vortex on the right hand moves clockwise and the one on the left anti-clockwise. At the centre of the pattern the air is seen rising towards the hot surface. The figure immediately suggests that the convection in the two vortices would tend to throw out a particle towards the hot surface on account of the centrifugal action whereas the repelling effect of the hot surface would act in the opposite way; the vortices appear to compress the dark space. The thickness of the dark space is only about 0·5 mm.

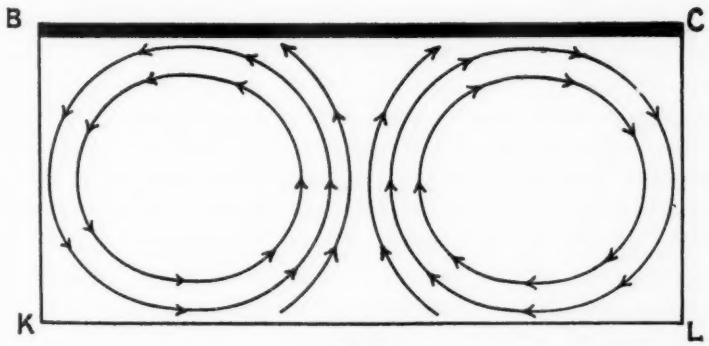


FIG. 3.

*Case* 2: *Separation between the surfaces* = 0·85 *cm.*—On decreasing the distance between B C and K L, the two vortices decrease in size, separate and move towards the two sides of the cell, as shown in Plate XI, Fig. 2. The air in the middle portion of the cell is free from any convectional movements, and here the repelling effect of the hot surface on the smoke particles

has its full sway. At the two ends of the cell the vortices, though smaller and less vigorous, still exercise a controlling effect, but even here the dark space is wider than in the previous case. The maximum width at the centre is of the order of 4 mm. Thus, a reduction in the distance between B C and K L from 2·29 cm. to 0·85 cm., *i.e.*, to a third of the original value has caused an increase in the width of the dark space from 0·5 mm. to 4 mm., *i.e.*, an eight-fold increase.

*Case* 3: *Separation between the surfaces* = 0·54 *cm.*—A further reduction of the distance between B C and K L brings about a rapid contraction of the vortices which now become very sluggish. The appearance of the pattern is shown in Plate XI, Fig. 3. The dark region now occupies the whole space between the two plates, the smoke being driven towards the cold surface everywhere except at the two ends where also, above the vortices, the dark space has widened still further.

The dark space at the centre which is equal to the distance between the two surfaces is now 5·4 mm.

*Case* 4: *Separation between the surfaces* = 0·34 *cm.*—Plate XI, Fig. 4 shows the pattern when the space is reduced to 0·34 cm. Smoke particles are absent everywhere except at the two ends where the last remnants of the two original vortices are just visible.

*Case* 5: *Separation between the surfaces* = 0·22 *cm.*—Lastly Plate XI, Fig. 5 shows the conditions when the distance between B C and K L is of the order 2·2 mm. At this distance smoke particles are driven away towards the cold surface as soon as they are introduced.

We thus see from Figs. 3, 4 and 5 of Plate XI that as soon as the hot surface comes to within 5 mm. of the cold surface the vortices and the movements associated with them tend to disappear. The controlling influence of convection being absent, the force of repulsion experienced by a particle near the hot surface continues to act on the particle until it is pushed away completely towards the cold surface.

There is a variation of the above series of experiments which leads to some further interesting results. The air in the space between B C and K L (Fig. 2) is kept free from smoke to start with. Hot water is poured into the upper vessel so as to heat the surface B C. After the air in the interspace has had time to take up the temperature gradient a puff of smoke is introduced gently through a narrow metal tube soldered to a small hole at the centre of B C. The puff of smoke does not show any trace of convection or tendency to spread sidewise if the distance between B C and K L is less than about 5 mm. The puff of smoke is seen to undergo a rapid vertical movement

downwards towards the cold plate B C, the upper boundary of the smoke layer being quite sharp. In the course of a few seconds all the smoke is repelled towards the cold surface and deposited on it.

The speed of the downward movement becomes more and more rapid as the distance between B C and K L is decreased. On the other hand, if the distance between them is increased to a centimetre or so, the downward movement becomes slower, the smoke partakes of the convectional movements which are associated with this distance between the two surfaces, and the upper boundary of the smoke layer remains at a distance of about 2 or 3 mm. away from the hot surface.

We thus see that the repulsion experienced by the smoke particles increases as the distance between the two surfaces is decreased. The fact that convective movements in the interspace are absolutely unnecessary to bring about a repulsion of the particles directly upsets the explanation offered by Lodge and Clarke, who supposed that a motion of the smoky air parallel to the hot surface is essential for the production of the dark layer (*loc. cit.*, pp. 234–39).

The above experiments with the two surfaces close to each other immediately suggest that we may investigate the phenomenon of the dark layer in a quantitative manner by measuring the rate at which the smoke layer* moves downwards away from the hot surface B C. The results of such a quantitative study when (1) the hot and the cold surfaces are maintained at definite temperatures, but the distance between them is varied and (2) the two surfaces are kept at a constant distance apart, but the temperature of the hot surface is varied, are described below.

The smoke was let into the cell (space between B C and K L) and the rate of movement of the smoke layer measured with the help of a stop-watch while another observer watched the movement of the smoke through a convex lens and an eye-piece provided with a graticule. The magnification of the optical system being known, the actual distances travelled by the smoke can be estimated readily.

(1) *Effect of changing the distance between the surfaces on the repulsion of the smoke layer.*—In this series of experiments the temperature of the upper surface B C was maintained at 70° C., *i.e.*, about 40° C. above that of the cold surface. The distance traversed by the smoke layer at various instants after its introduction into the cell was recorded when the separation between B C and K L was 9·0 mm., 6·0 mm and 3·5 mm. respectively. These observations

* By the "smoke layer" we shall hereafter mean the sharp upper surface of the smoke layer.

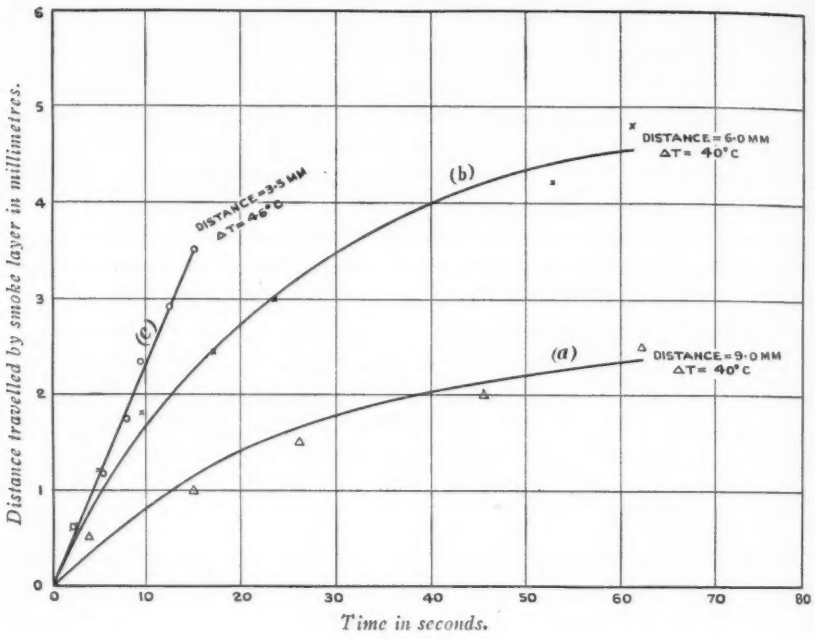


FIG. 4.

are plotted in curves (*a*), (*b*) and (*c*) in Fig. 4. From these curves we see that the rate of movement of the smoke layer was most rapid as well as uniform when the hot and the cold surfaces were nearest to each other. For example the velocity indicated by curve (*c*) is larger than that indicated by either (*a*) or (*b*) in Fig. 4, and the distance—time relation is represented by a straight line ; when the distance between the hot and the cold surfaces is increased, the particles of smoke move at smaller velocities and also less and less rapidly as they recede from the hot surface. The velocities attained by the smoke layer at different distances away from the hot surface were calculated from the curves in Fig. 4 and are given in Table II below.

The falling away of the velocity as the particles move away from the hot surface when the thickness of the air cell is 0·6 cm. or more shows that the opposing influence of convection begins to be felt in these cases. When the thickness of the air cell is 0·35 cm. or less the particles move with a uniform velocity throughout their passage from the hot to the cold surface ; in this case convection of the air in the cell is absent as we have already seen.

(2) *Effect of changing the temperature difference between the hot and the cold surfaces while keeping the distance between them constant.*—From the

TABLE II.

| Distance between hot surface B C and cold surface K L in cm. | Distance of smoke layer from the hot surface in cm. | Velocity of the smoke layer in cm./sec. |
|---|---|---|
| 0·90 | 0·05 | 0·0083 |
| | 0·15 | 0·0034 |
| | 0·24 | 0·0000 |
| 0·60 | 0·05 | 0·0182 |
| | 0·15 | 0·0143 |
| | 0·25 | 0·0111 |
| | 0·35 | 0·0054 |
| | 0·46 | 0·0000 |
| 0·35 | 0·05 | 0·0226 |
| | 0·15 | 0·0226 |
| | 0·25 | 0·0226 |
| | 0·35 | 0·0226 |

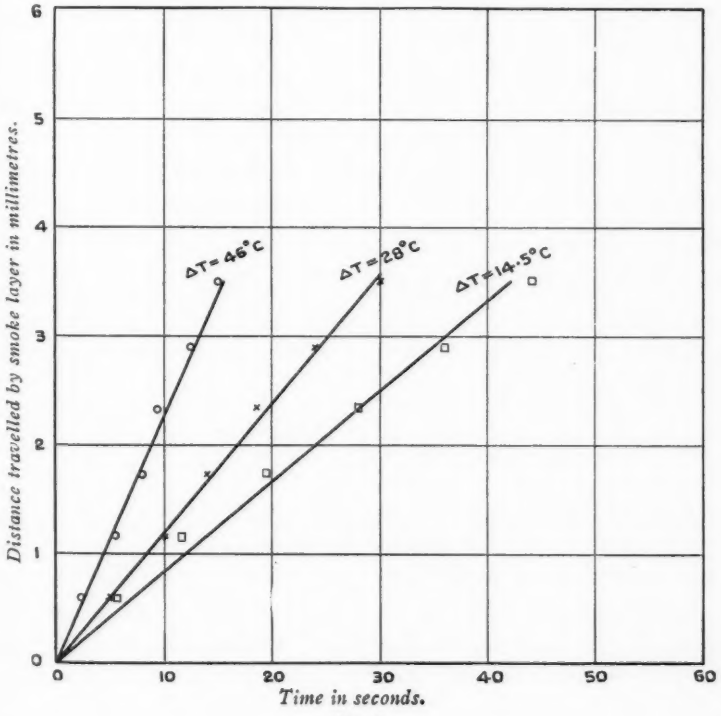


FIG. 5.

previous section it is clear that the experiments for detecting the variation of velocity with temperature gradient will be most instructive when the hot and cold surfaces are kept at 0·35 cm. or less from each other. In this case the smoke travels with a uniform velocity and the dark layer occupies the whole space between the two surfaces.

The temperature differences $\Delta T$ between the hot and the cold surfaces were adjusted to be 46° C., 28° C. and 14°·5 C. respectively and the rate of movement of the smoke layer measured as before. These measurements have been plotted in Fig. 5. The graph of distance traversed ($d$) against time is a straight line in each case. The mean velocities of movement of the smoke for different values of the temperature gradient as calculated from these graphs are given in Table III below.

TABLE III.

| Temperature gradient in °C. per cm. $\left(\frac{\Delta T}{d}\right)$ | Mean velocity of the smoke layer in cm./sec. |
|---|---|
| 131 | ·0226 |
| 80 | ·0119 |
| 41 | ·0083 |

From the above values a graph of velocity against temperature gradient has been drawn (see Fig. 6). It is interesting to note that the graph is nearly linear. The relation between velocity ($v$) and temperature gradient $\frac{\Delta T}{d}$ may be expressed as

$$v = 1{\cdot}756 \times 10^{-4} \times \frac{\Delta T}{d}.$$

Having established that in the above experiments (where convection in the air cell is eliminated by bringing the hot and cold surfaces sufficiently close to each other) the smoke particles move with a velocity proportional to the temperature gradient, we may now discuss how this result may be utilised for computing the force of repulsion experienced by a smoke particle in the neighbourhood of a hot surface.

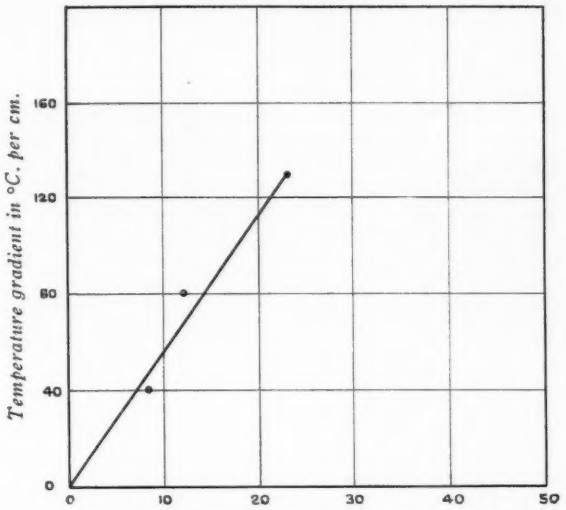


FIG. 6.

*4. Calculation of the repulsive force experienced by a smoke particle in the neighbourhood of a hot surface.*

From a knowledge of the velocity of a smoke particle we can estimate the force of repulsion experienced by it when it is near a hot surface.

For the free fall of a spherical particle of radius $r$ under the influence of gravity the limiting velocity (according to Stokes' law[7]) is given by

$$6\,\pi\eta r v' = \tfrac{4}{3}\pi r^3 (\rho - \rho')\, g \text{ or}$$

$$v' = \tfrac{2}{9}\,\frac{r^2 (\rho - \rho')\, g}{\eta} \qquad \ldots\ \ldots\ \ldots\ \ldots\ \ldots \quad (1)$$

where

$v'$ is the limiting velocity of the particle,

$\rho$ is the density of the particle,

$\rho'$ is the density of air,

$g$ is the acceleration due to gravity, and

$\eta$ is the viscosity coefficient of air.

If, in addition to gravity there is an additional force F (to which the influence of the hot surface may be considered as being equivalent) in the same direction, the limiting velocity $v''$ is given by

$$6\,\pi\eta r v'' = \mathrm{F} + \tfrac{4}{3}\pi r^3 (\rho - \rho')\, g$$

so that

$$\frac{v''}{v'} = \frac{F + \frac{4}{3}\pi r^3 (\rho - \rho') g}{\frac{4}{3}\pi r^3 (\rho - \rho') g}.$$

If the size of the particle is small compared to the mean free path[8,9] $\lambda$, the limiting velocities $v'$ and $v''$ will be altered to $v_1$ and $v_2$ which are given by

$$\left.\begin{aligned} v_1 &= v'\left(1 + K\frac{\lambda}{r}\right) \\ \text{and} \quad v_2 &= v''\left(1 + K\frac{\lambda}{r}\right) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where K is a constant equal to 0·86 and $\lambda = 6{\cdot}32 \times 10^{-6}$ for air at N. T. P. From (2) we have

$$\frac{v_2}{v_1} = \frac{v''}{v'} \text{ so that}$$

$$\frac{v_2 - v_1}{v_1} = \frac{F}{\frac{4}{3}\pi r^3 (\rho - \rho') g} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

Let us consider the case where the hot and the cold surfaces are at 75° C. and 29° C. respectively and 3·5 mm. apart. The values of $\eta$ at these temperatures are $2{\cdot}090 \times 10^{-4}$ and $1{\cdot}875 \times 10^{-4}$ c.g.s. units respectively so that for a mean temperature of 52° C. of the air between the two surfaces we have a mean value of $\eta$ equal to $1{\cdot}98 \times 10^{-4}$. Neglecting $\rho'$ and putting $r = 2{\cdot}5 \times 10^{-5}$ cm. (results of our measurements) and $\rho = 2{\cdot}3$ (density of carbon) we have from equations (1) and (2)

$$v_1 = 1{\cdot}93 \times 10^{-3} \text{ cm./sec.}$$

From our measurements we know that for this particular case $v_2$ was equal to $22{\cdot}6 \times 10^{-3}$ cm./sec. so that substituting in equation (3) we have

$$\frac{F}{\frac{4}{3}\pi r^3 \rho g} = \frac{(22{\cdot}6 - 1{\cdot}93) \times 10^{-3}}{1{\cdot}93 \times 10^{-3}} = 10{\cdot}71.$$

$$\therefore F = \tfrac{4}{3}\pi r^3 \rho g \times 10{\cdot}71$$

The excess of pressure $\Delta P$ exerted by the particle on account of this extra force due to a temperature gradient of 131° C. per cm., will be

$$\Delta P = \frac{F}{\pi r^2} = \tfrac{4}{3}\pi r^3 \rho \times \frac{10{\cdot}71 g}{\pi r^2}$$

$$= 0{\cdot}81 \text{ dyne/cm.}^2$$

This excess of pressure is due to the more vigorous impacts on the side of the particle facing the hot surface than on the side facing the cold surface. The pressure is too small to be detected by ordinary methods but is sufficiently large to affect the small particles we are considering.

FIG. 1.

FIG. 3.

FIG. 2.

FIG. 4.

FIG. 5.

Development of the dark layer as convection in the air cell is decreased by bringing the hot and the cold surfaces together.

*Summary.*

The paper discusses the formation of the dark or dust-free layer in the space between a hot surface (above) and a cold surface (below). The variations of the dark layer (1) with distance between the surfaces when the temperatures of the two surfaces are kept unaltered and (2) with the temperature gradient when the distance is kept constant at 3·5 mm. have been studied. It is shown that when the distance between the two surfaces is less than 4 mm. the whole space is occupied by the dark layer. If smoke is introduced into this space it travels from the hot to the cold surface with a velocity proportional to the temperature gradient. The excess of pressure associated with the velocity of the particle is calculated.

*Conclusion.*

These investigations are being continued at different pressures and with particles of different sizes. The applications of interferometry to the study of the phenomena near a hot surface will be discussed in the next part of this series.

In conclusion, the author has great pleasure in expressing his best thanks to the Director-General of Observatories for facilities given at the laboratories of the Meteorological Office at Poona and to Dr. L. A. Ramdas for his guidance.

REFERENCES.

1. Tyndall, *Proceedings of the Royal Institute,* London, 1870, **6**, 1.
2. Rayleigh, *Proceedings of the Royal Society,* December 1882.
3. Aitken, *Transactions of the Royal Society,* Edinburgh, 1884, **32**.
4. Lodge, O. J., and Clark, J. W., *Philosophical Magazine,* 1884, **17**.
5. Hooper, W. J., *Physics,* 1931, **1**, No. 1.
6. Ramdas, L. A., and Malurkar, S. L., *Indian Journal of Physics,* 1932, **7**, part 1.
7. Stokes, *Mathematical and Physical Papers,* 1901, **3**, 59.
8. Cunningham, *Proceedings of the Royal Society,* 1910, **83A**, 357.
9. Millikan, *Phys. Zeit.,* 1910, **11**, 1097.

# SEMI-VECTORS IN BORN'S FIELD THEORY.

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## *1. Introduction.*

In their first paper[1] on the quantisation of the field equations of the new field theory, Born and Infeld showed that there are four possible standpoints for the choice of the action function needed to develop the field theory. These correspond to the four ways of choosing the primary field vectors (one electric and one magnetic) from among $\vec{E}$, $\vec{D}$, $\vec{H}$, $\vec{B}$, *viz.*, $\vec{E}$, $\vec{B} - \vec{D}$, $\vec{H} - \vec{D}$, $\vec{B} - \vec{E}$, $\vec{H}$. In each case there exists an action function from which the complementary pair can be derived by differentiation. In the first two cases the action functions were respectively the Lagrangian L $(\vec{B}, \vec{E})$ and the Hamiltonian H $(\vec{D}, \vec{H})$ and Born and Infeld have shown in an earlier paper[2] that in both these cases the action functions can be explicitly put, using the antisymmetrical tensors $f_{kl}$ and $p_{kl}$, in an invariant form and similarly that the relations connecting primary and secondary vectors can be exhibited in a Lorentz-invariant form using tensor notation.

The other two methods of choice which correspond to U $(\vec{D}, \vec{B})$ the energy-density and V $(\vec{E}, \vec{H})$ mean the splitting of the antisymmetrical tensors and hence the abandonment of the four dimensional tensor notation. It is however necessary for the relativistic invariance of the new field theory that the relations

$$\vec{E} = \frac{\partial U}{\partial \vec{D}}, \quad \vec{H} = \frac{\partial U}{\partial \vec{B}}$$

and

$$\vec{D} = -\frac{\partial V}{\partial \vec{E}}, \quad \vec{B} = -\frac{\partial V}{\partial \vec{H}}$$

should be Lorentz-invariant. We show in this paper that the above relations and consequently the field equations derived from U and V are invariant

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[1] Born and Infeld, *Proc. Roy. Soc.*, A, 1934, **147**, 522.

[2] *Proc. Roy. Soc.*, A, 1934, **144**, 425.

against Lorentz-transformations although U and V themselves are not Lorentz-invariant. For this purpose we employ the (B)- and (C)-transformations of Einstein and Mayer's semi-vector theory[3] and show that the first set of the above relations are invariant against the (B)- and the second set against the (C)-transformations.

The conditions $(\vec{B} \times \vec{H}) + (\vec{D} \times \vec{E}) = 0$, and $(\vec{D} \times \vec{B}) = (\vec{E} \times \vec{H})$ which are necessary for the relativistic invariance[4] of the field theory are examined for invariance under the above transformations and it is shown that while the first condition is invariant only under the (B)-transformations the second is so under both.

The several invariants are expressed in spinor notation and it is shown therefrom that U and V are not spinor invariants.

### 2. *U and V not Lorentz-invariant.*

The Lagrangian $L = L(\vec{B}^2 - \vec{E}^2, \vec{B}\cdot\vec{E}) = L(F, G)$ and the Hamiltonian $H = H(\vec{D}^2 - \vec{H}^2, \vec{D}\cdot\vec{H}) = H(P, Q)$ are Lorentz-invariant since F, G, P and Q are tensor invariant but

$$U = L + (\vec{D}\cdot\vec{E})$$

and $$V = L - (\vec{B}\cdot\vec{H})$$

are not Lorentz-invariant since $(\vec{D}\cdot\vec{E})$ and $(\vec{B}\cdot\vec{H})$ are not so being merely space-invariants.

### 3. *U and V not spinor-invariant.*

We can also prove that U and V are not Lorentz-invariant by showing that they are not spinor invariants. Using the notation of Laporte and Uhlenbeck[5] let

$$G^{kl} = f^{kl} + f^{*kl} \quad \text{(using the Minkowski line element)}$$

be a self-dual antisymmetric tensor. We have

$$\begin{cases} G_{23} = f_{23} - if_{14}, \cdots \\ G_{14} = f_{14} + if_{23}, \cdots \end{cases} \qquad \begin{pmatrix} (f_{23}, f_{31}, f_{12}) \to \vec{B} \\ (f_{14}, f_{24}, f_{34}) \to \vec{E} \end{pmatrix}$$

such that the relations

$$G_{23} = -iG_{14}, \ldots\ldots\ldots$$
$$G_{14} = iG_{23}, \ldots\ldots\ldots \text{ are satisfied.}$$

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[3] Einstein and Mayer, *Berl. Ber.*, 1932, 522.

[4] See Born and Infeld, *Proc. Roy. Soc.*, A, 1935, **150**, 159.

[5] Laporte and Uhlenbeck, *Phys. Rev.*, 1931, **38** (II), 1380.

Denoting the "*Kenn-zahlen*" of $G^{kl}$ by $k_1, k_2, k_3$ we can write

$$G^{kl} = \begin{pmatrix} 0 & k_3 & -k_2 & -ik_1 \\ -k_3 & 0 & k_1 & -ik_2 \\ k_2 & -k_1 & 0 & -ik_3 \\ ik_1 & ik_2 & ik_3 & 0 \end{pmatrix}$$

from which we easily deduce $G_{23} = -k_1 = f_{23} - if_{14}$; $G_{31} = -k_2 = f_{31} - if_{24}$; $G_{12} = k_3 = f_{12} - if_{34}$.

We can associate with $G^{kl}$ the two conjugate symmetric spinors $g_{rs}$ and $g^{\dot{r}\dot{s}}$ whose elements are given by

$$g_{\dot{1}\dot{1}} = 2(k_2 + ik_1); \quad g_{\dot{2}\dot{2}} = 2(k_2 - ik_1); \quad g_{\dot{1}\dot{2}} = g_{\dot{2}\dot{1}} = -2ik_3$$

$$g_{11} = 2(\bar{k}_2 - i\bar{k}_1); \quad g_{22} = 2(\bar{k}_2 + i\bar{k}_1); \quad g_{12} = g_{21} = 2i\bar{k}_3.$$

We can form the two spinor-invariants

$$g_{rs}\, g^{rs} \text{ and } g_{\dot{r}\dot{s}}\, g^{\dot{r}\dot{s}}.$$

$$g_{rs}\, g^{rs} = g_{11}\, g^{11} + g_{12}\, g^{12} + g_{21}\, g^{21} + g_{22}\, g^{22} = 2(g_{11}\, g_{22} - g_{12}^2)$$

$$\therefore \quad \tfrac{1}{8}\, g_{rs}\, g^{rs} = (\bar{k}_2 - i\bar{k}_1)(\bar{k}_2 + i\bar{k}_1) - (i\bar{k}_3)^2 = \bar{k}_1^2 + \bar{k}_2^2 + \bar{k}_3^2$$

$$= (f_{23} + if_{14})^2 + (f_{31} + if_{24})^2 + (f_{12} + if_{34})^2$$

$$= F + 2iG.$$

In exactly the same way, we have

$$\tfrac{1}{8}\, g_{\dot{r}\dot{s}}\, g^{\dot{r}\dot{s}} = k_1^2 + k_2^2 + k_3^2 = F - 2iG$$

which proves the invariance of F and G.

Next consider, $H^{kl} = p^{kl} + p^{*kl}$ $\quad \begin{pmatrix} p_{23}, p_{31}, p_{12} \to \vec{H} \\ p_{14}, p_{24}, p_{34} \to \vec{D} \end{pmatrix}$

and associate the spinors $h_{rs}$ and $h^{\dot{r}\dot{s}}$ defined by $l_1, l_2, l_3$. The invariants $h_{rs}\, h^{rs}$ and $h_{\dot{r}\dot{s}}\, h^{\dot{r}\dot{s}}$ give exactly as above the two spinor-invariants

$$\tfrac{1}{8}\, h_{rs}\, h^{rs} = P + 2iQ$$

$$\tfrac{1}{8}\, h_{\dot{r}\dot{s}}\, h^{\dot{r}\dot{s}} = P - 2iQ$$

which proves the invariance of P and Q.

We can also consider the mixed invariants

$$g_{rs}\, h^{rs} \text{ and } g_{\dot{r}\dot{s}}\, h^{\dot{r}\dot{s}}.$$

We have

$$g_{rs}\, h^{rs} = g_{11}\, h^{11} + g_{12}\, h^{12} + g_{21}\, h^{21} + g_{22}\, h^{22} = g_{11}\, h_{22} + g_{22}\, h_{11} - 2g_{12}\, h_{12}$$

*i.e.*, $\tfrac{1}{4}\, g_{rs}\, h^{rs} = (\bar{k}_2 - i\bar{k}_1)(\bar{l}_2 + i\bar{l}_1) + (\bar{k}_2 + i\bar{k}_1)(\bar{l}_2 - i\bar{l}_1) - 2(i\bar{k}_3)(i\bar{l}_3)$

and $\tfrac{1}{8}\, g_{rs}\, h^{rs} = \bar{k}_1\, \bar{l}_1 + \bar{k}_2\, \bar{l}_2 + \bar{k}_3\, \bar{l}_3 = (f_{23} - if_{14})(p_{23} - ip_{14}) + \cdots$

$$= (\vec{B}\vec{H} - \vec{E}\vec{D}) - i(\vec{B}\vec{D} + \vec{E}\vec{H}).$$

In exactly the same way, we find

$$\tfrac{1}{8}\, g_{\ddot{r}\ddot{s}}\, h^{\ddot{r}\ddot{s}} = k_1 l_1 + k_2 l_2 + k_3 l_3$$
$$= (\vec{\vec{B}}\vec{\vec{H}} - \vec{\vec{E}}\vec{\vec{D}}) + i\,(\vec{\vec{B}}\vec{\vec{D}} + \vec{\vec{E}}\vec{\vec{H}})$$

which proves the invariance of $(\vec{\vec{B}}\vec{\vec{H}} - \vec{\vec{E}}\vec{\vec{D}})$; $(\vec{\vec{B}}\vec{\vec{D}} + \vec{\vec{E}}\vec{\vec{H}})$.

We have so far proved that $(\vec{B}^2 - \vec{E}^2)$, $(\vec{\vec{B}}\vec{\vec{E}})$; $(\vec{H}^2 - \vec{D}^2)$, $(\vec{\vec{H}}\vec{\vec{D}})$; $(\vec{\vec{B}}\vec{\vec{H}} - \vec{\vec{E}}\vec{\vec{D}})$ and $(\vec{\vec{B}}\vec{\vec{D}} + \vec{\vec{E}}\vec{\vec{H}})$ are spinor-invariants but these are also tensor invariants as evident from the following forms

$$\left.\begin{aligned}
&\vec{B}^2 - \vec{E}^2 = \tfrac{1}{2} f_{kl} f^{kl};\ (\vec{\vec{B}}\vec{\vec{E}}) = 1/4\, f_{sk} f^{*sk} \\
&\vec{D}^2 - \vec{H}^2 = \tfrac{1}{2} p^{*kl} p_{kl}^{\ *} = \tfrac{1}{2} p_{kl} p^{kl};\ (\vec{\vec{H}}\vec{\vec{D}}) = 1/4\, p^{sk} p_{sk}^{\ *} \\
&\vec{\vec{B}}\vec{\vec{H}} - \vec{\vec{E}}\vec{\vec{D}} = \tfrac{1}{2} p^{kl} f_{kl}\ \vec{\vec{B}}\vec{\vec{D}} + \vec{\vec{E}}\vec{\vec{H}} = \tfrac{1}{2} p^{*kl} f_{kl}
\end{aligned}\right\}$$

In terms of $k_1$, $k_2$, $k_3$ and $l_1$, $l_2$, $l_3$ these invariants are derived from the forms

$$k_1^2 + k_2^2 + k_3^2;\ \bar{k}_1^2 + \bar{k}_2^2 + \bar{k}_3^2;\ l_1^2 + l_2^2 + l_3^2;\ \bar{l}_1^2 + \bar{l}_2^2 + \bar{l}_3^2,$$
$$k_1 l_1 + k_2 l_2 + k_3 l_3 \text{ and } \bar{k}_1 \bar{l}_1 + \bar{k}_2 \bar{l}_2 + \bar{k}_3 \bar{l}_3.$$

We can now form the four expressions

$$k_1 \bar{k}_1 + k_2 \bar{k}_2 + k_3 \bar{k}_3;\ l_1 \bar{l}_1 + l_2 \bar{l}_2 + l_3 \bar{l}_3$$
$$\bar{k}_1 l_1 + \bar{k}_2 l_2 + \bar{k}_3 l_3;\ k_1 \bar{l}_1 + k_2 \bar{l}_2 + k_3 \bar{l}_3$$

which reduce to

$$\vec{B}^2 + \vec{E}^2;\ \vec{H}^2 + \vec{D}^2;\ (\vec{\vec{B}}\vec{\vec{H}} + \vec{\vec{E}}\vec{\vec{D}}) + i(\vec{\vec{E}}\vec{\vec{H}} - \vec{\vec{B}}\vec{\vec{D}});\ (\vec{\vec{B}}\vec{\vec{H}} + \vec{\vec{E}}\vec{\vec{D}}) - i(\vec{\vec{E}}\vec{\vec{H}} - \vec{\vec{B}}\vec{\vec{D}}).$$

These are not however spinor-invariants since they correspond to the forms $g_{rs} g^{\ddot{r}\ddot{s}}$; $h_{rs} h^{\ddot{r}\ddot{s}}$; $g_{rs} h^{\ddot{r}\ddot{s}}$; $g^{\ddot{r}\ddot{s}} h^{rs}$ and contraction of dotted and undotted indices does not give such an invariant. Thus $\vec{\vec{B}}\vec{\vec{H}} + \vec{\vec{E}}\vec{\vec{D}}$ is not a spinor-invariant while $\vec{\vec{B}}\vec{\vec{H}} - \vec{\vec{E}}\vec{\vec{D}}$ is so. Hence $(\vec{\vec{D}}\vec{\vec{E}})$ and $(\vec{\vec{B}}\vec{\vec{H}})$ are not spinor, *i.e.*, Lorentz-invariants and the same is consequently true of U and V.

### 4. *Semi-Vectors.*

We will give here those parts of the Einstein-Mayer theory of semi-vectors which will be used in the present investigation. Since Einstein-Mayer use the Minkowski line-element we shall transfer the results to the case of the line element used in the field theory.

According to the line-element used in the Born-Infeld theory we have the relation

$$(h_{ik}^{\ *})^* = -\, h_{ik}$$

so that, if $h_{ik}^{\ *} = a h_{ik}$.

We easily derive $a^2 = -1$, *i.e.*, $a = \pm i$; and, hence the self-dual and anti-dual antisymmetric tensors are defined by

$$u_{ik}^{*} = iu_{ik} \text{ and } v_{ik}^{*} = -iv_{ik}$$

and using the rule of pulling the indices up and down

$$\left.\begin{aligned} u_{23} &= -iu_{14};\ u_{14} = iu_{23}, \text{ etc.} \\ v_{23} &= iv_{14};\ v_{14} = -iv_{23}, \text{ etc.} \end{aligned}\right\}$$

just as in the Einstein-Mayer theory. The special antisymmetric $u$'s and $v$'s form a linear space and because of this linearity any $u_{ik}$ (or $v_{ik}$) can be expressed in terms of three suitably chosen $u_{ik}$'s (or $v_{ik}$'s). Let us take $\underset{1}{u}_{ik}$ defined such that all except $\underset{1}{u}_{23}$ is equal to zero, but $\underset{1}{u}_{23} = -iu_{14} = 1$ with $\underset{2}{u}_{ik}$ and $\underset{3}{u}_{ik}$ similarly defined. We can then form any $u_{ik}$ by

$$\left.\begin{aligned} u_{ik} &= \alpha_1 \underset{1}{u}_{ik} + \alpha_2 \underset{2}{u}_{ik} + \alpha_3 \underset{3}{u}_{ik} \\ \text{and similarly} \quad v_{ik} &= \beta_1 \underset{1}{v}_{ik} + \beta_2 \underset{2}{v}_{ik} + \beta_3 \underset{3}{v}_{ik} \end{aligned}\right\}$$

where $\alpha_1, \alpha_2, \alpha_3$ and $\beta_1, \beta_2, \beta_3$ are quite arbitrary. We can thus write

$$\left.\begin{aligned} u_{23} &= \alpha_1,\ u_{31} = \alpha_2,\ u_{12} = \alpha_3,\ u_{14} = i\alpha_1, \cdots \\ v_{23} &= \beta_1,\ v_{31} = \beta_2,\ v_{12} = \beta_3,\ v_{14} = -i\beta_1, \cdots \end{aligned}\right\} \quad \ldots \quad \ldots \quad (1)$$

Let $(a_{ik})$ be the group (D) of rotations constituting the Lorentz-group and let us write

$$a_{ik} = b_{i\rho}\, c_k^{\rho}$$

where $(b_{ik})$, $(c_{ik})$ are two sub-groups of the Lorentz-group and also isomorphous with $(a_{ik})$. The condition for the existence of such a factorisation is that the $b$- and $c$-rotations be "*vertauschbar*". When this condition is satisfied and when $c_{ik}$ is taken as the infinitesimal rotation

$$c_{ik} = g_{ik} + v_{ik}$$

we can determine $b_{ik}$ from the necessary consequence that $(b_{ik})$ is "*austachbar*" with $(v_{ik})$. We can find for $b_{ik}$ the form

$$b_{ik} = bg_{ik} + u_{ik}$$

where $b = b_{11} = b_{22} = b_{33} = -b_{44}$. In general the $(b_{ik})$ so determined will not be a "*Drehung*" and will be one if

$$b^2 + \tfrac{1}{4}\, u_{ik}\, u^{ki} = 1.$$

The group of rotations in $(b_{ik})$, *i.e.*, those satisfying the above condition is denoted by (B) and is the greatest common measure of $(a_{ik})$ and $(b_{ik})$. We can similarly define the sub-group of rotations (C).

An infinitesimal element of the group $(b_{ik})$ is given by $g_{ik}\ (1 + \delta b) + \delta u_{ik}$ $(b_{ik} = bg_{ik} + u_{ik})$ and the condition, for this being a rotation, *viz.*,

$b^2 + \frac{1}{4} u_{ik} u^{ki} = 1$, becomes

$$(1 + \delta b)^2 + \tfrac{1}{4} \delta u_{ik} \delta u^{ik} = 1 \text{ or } \delta b = 0.$$

Hence an infinitesimal element of (B) is $g_{ik} + \delta u_{ik}$; similarly an infinitesimal element of the group (C) is given by

$g_{ik} + \delta v_{ik}$, *i.e.*, by

$$\left.\begin{aligned} b_{ik} &= g_{ik} + \delta u_{ik} \\ c_{ik} &= g_{ik} + \delta v_{ik} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

*5. Equations of transformation.*

The equations connecting field quantities[6] can be written in the form,

$$\left.\begin{aligned} \vec{E} &= \frac{\vec{D}\,(1 + \vec{B}^2) - \vec{B}R}{\sqrt{(1 + \vec{D}^2)\,(1 + \vec{B}^2) - R^2}} \\ \vec{H} &= \frac{\vec{B}\,(1 + \vec{D}^2) - \vec{D}R}{\sqrt{(1 + \vec{D}^2)\,(1 + \vec{B}^2) - R^2}} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where $U = \sqrt{(1 + \vec{D}^2)\,(1 + \vec{B}^2) - R^2}$, and $R = (\vec{D} \cdot \vec{B})$.

We will show that the equations (3) are invariant with respect to transformations of the group (B) and thus establish their Lorentz-invariance. Since group (B) consists of rotations, it is sufficient to consider only infinitesimal elements of the group.

Let us denote by

$$x^1, x^2, x^3, x^4 \longrightarrow x, y, z, t$$
$$x^{1'}, x^{2'}, x^{3'}, x^{4'} \longrightarrow x', y', z', t'$$

the co-ordinates of world-points in systems $\Sigma$ and $\Sigma'$ connected by infinitesimal transformations defined by (2).

In consonance with (2) we can write such a transformation as

$$x'^{\mu} = g_{\nu}{}^{\mu}\, x^{\nu} + \delta u_{\nu}{}^{\cdot\mu}\, x^{\nu} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

such that $g_{\nu}{}^{\mu} = \begin{cases} 1 \text{ if } \mu = \nu \\ 0 \text{ if } \mu \neq \nu \end{cases}$

and the dot in $u_{\nu}{}^{\cdot\mu}$ denotes the order of the indices. The tensor components $f_{ik}$ and $p_{ik}$ are derived from the transformation rules of tensors. Thus,

$$\left.\begin{aligned} f'_{14} &= (g_1{}^{\nu} + \delta u_1{}^{\nu})\,(g_4{}^{\rho} + \delta u_4{}^{\rho})\, f_{\nu\rho} = f_{14} + \delta u_1{}^{\nu} f_{\nu 4} + \delta u_4{}^{\nu} f_{1\nu} \\ f'_{23} &= (g_2{}^{\nu} + \delta u_2{}^{\nu})\,(g_3{}^{\rho} + \delta u_3{}^{\rho})\, f_{\nu\rho} = f_{23} + \delta u_2{}^{\nu} f_{\nu 3} + \delta u_3{}^{\nu} f_{2\nu} \end{aligned}\right\}$$

where, in consequence of the infinitesimal nature of the transformation, we

[6] Born and Infeld, Ref. (1), p. 525, formula (2.7A).

neglect the coefficient of the second power of $\delta$. Writing these in the expanded form, we get

$$\left.\begin{aligned} f'_{14} &= f_{14} + \delta\alpha_2 (f_{34} + if_{12}) - \delta\alpha_3 (f_{24} + if_{31}) \\ f'_{23} &= f_{23} + \delta\alpha_2 (f_{12} - if_{34}) - \delta\alpha_3 (f_{31} - if_{24}) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (5)$$

making using of (1). Introducing a space-vector $\vec{a}$ whose components are $(a_1, a_2, a_3)$ these equations can be written as

$$\left.\begin{aligned} \vec{E}' &= \vec{E} + i\delta\ (\vec{a} \times \overrightarrow{B - iE})\ ;\ \vec{B}' = \vec{B} + \delta\ (\vec{a} \times \overrightarrow{B - iE}) \\ \vec{D}' &= \vec{D} + i\delta\ (\vec{a} \times \overrightarrow{H - iD})\ ;\ \vec{H}' = \vec{H} + \delta\ (\vec{a} \times \overrightarrow{H - iD}) \end{aligned}\right\} \quad .. \quad (6)$$

the second set in (6) being obtained by the transformation of the components of the tensor $p_{kl}$. Dealing with the (C)-Lorentz-transformation in a similar way we have the equations of transformation

$$\left.\begin{aligned} f'_{14} &= f_{14} - i\delta\beta_2 (f_{12} + if_{34}) + i\delta\beta_3 (f_{31} + if_{24}) \\ f'_{23} &= f_{23} + \delta\beta_2 (f_{12} + if_{34}) - \delta\beta_3 (f_{31} + if_{24}) \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (5')$$

or taking $\vec{\beta} \to (\beta_1, \beta_2, \beta_3)$,

$$\left.\begin{aligned} \vec{E}' &= \vec{E} - i\delta\ (\vec{\beta} \times \overrightarrow{B + iE})\ ;\ \vec{B}' = \vec{B} + \delta\ (\vec{\beta} \times \overrightarrow{B + iE}) \\ \vec{D}' &= \vec{D} - i\delta\ (\vec{\beta} \times \overrightarrow{H + iD})\ ;\ \vec{H}' = \vec{H} + \delta\ (\vec{\beta} \times \overrightarrow{H + iD}) \end{aligned}\right\} \quad .. \quad (6')$$

### 6. *Lorentz-invariance of the conditions.*

$$(\vec{E} \times \vec{H}) - (\vec{D} \times \vec{B}) = 0\ ;\ (\vec{E} \times \vec{D}) + (\vec{H} \times \vec{B}) = 0.$$

Before proceeding to prove the invariance of the equations (3) we will consider the transformation of the above two conditions

$$(\vec{E} \times \vec{H}) - (\vec{D} \times \vec{B}) = 0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

and $$(\vec{E} \times \vec{D}) + (\vec{H} \times \vec{B}) = 0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

under (6) and (6'). The conditions (7) and (8) are intimately connected with the question of the Lorentz-invariance of the field equations derived from U. In fact, it is known [*cf.*, Born-Infeld, Reference (4)] that the former is a necessary and sufficient condition while the latter is a necessary one only. We will now show that (7) remains invariant under both the (B)- and (C)-transformations while (8) does so only under the (B)-transformation. Under transformation (6),

$$\begin{aligned} (\vec{D}' \times \vec{B}') - (\vec{E}' \times \vec{H}') = &\left\{\vec{D} + i\delta\ (\vec{a} \times \overrightarrow{H - iD})\right\} \times \left\{\vec{B} + \delta\ (\vec{a} \times \overrightarrow{B - iE})\right\} \\ &- \left\{\vec{E} + i\delta\ (\vec{a} \times \overrightarrow{B - iE})\right\} \times \left\{\vec{H} + \delta\ (\vec{a} \times \overrightarrow{H - iD})\right\} \end{aligned}$$

$$= \delta \vec{D} \times (\vec{a} \times \overrightarrow{B - iE}) - i\delta \vec{B} \times (\vec{a} \times \overrightarrow{H - iD}) - \delta \vec{E} \times (\vec{a} \times \overrightarrow{H - iD}) + i\delta \vec{H} \times (\vec{a} \times \overrightarrow{B - iE})$$

[(since $(\vec{D} \times \vec{B}) - (\vec{E} \times \vec{H}) = 0$ from (8)]

$$= i\delta \left\{ \vec{E} (\vec{D} \cdot \vec{a}) - \vec{D} (\vec{E} \cdot \vec{a}) \right\} + i\delta \left\{ \vec{H} (\vec{B} \cdot \vec{a}) - \vec{B} (\vec{H} \cdot \vec{a}) \right\} + \delta \left\{ \vec{H} (\vec{E} \cdot \vec{a}) - \vec{E} (\vec{H} \cdot \vec{a}) \right\} + \delta \left\{ \vec{D} (\vec{B} \cdot \vec{a}) - \vec{B} (\vec{D} \cdot \vec{a}) \right\}$$

[since all terms in $\vec{a}$ cancel out]

$$= i\delta \vec{a} \times (\vec{E} \times \vec{D}) + i\delta \vec{a} \times (\vec{H} \times \vec{B}) + \delta \vec{a} \times (\vec{H} \times \vec{E}) + \delta \vec{a} \times (\vec{D} \times \vec{B})$$

$= 0$, using (7) and (8).

Under transformation (6′),

$$(\vec{D}' \times \vec{B}') - (\vec{E}' \times \vec{H}')$$

$$= i\delta \vec{B} \times (\vec{\beta} \times \overrightarrow{H + iD}) - i\delta \vec{H} \times (\vec{\beta} \times \overrightarrow{B + iE}) + \delta \vec{D} \times (\vec{\beta} \times \overrightarrow{B + iE}) - \delta \vec{E} \times (\vec{\beta} \times \overrightarrow{H + iD})$$

$$= i\delta \left\{ \vec{B} (\vec{H} \cdot \vec{\beta}) - \vec{H} (\vec{B} \cdot \vec{\beta}) \right\} + i\delta \left\{ \vec{D} (\vec{E} \cdot \vec{\beta}) - \vec{E} (\vec{D} \cdot \vec{\beta}) \right\} + \delta \left\{ \vec{H} (\vec{E} \cdot \vec{\beta}) - \vec{E} (\vec{H} \cdot \vec{\beta}) \right\} + \delta \left\{ \vec{D} (\vec{B} \cdot \vec{\beta}) - \vec{B} (\vec{D} \cdot \vec{\beta}) \right\}$$

$$= i\delta \vec{\beta} \times \left\{ (\vec{B} \times \vec{H}) + (\vec{D} \times \vec{E}) \right\} + \delta \vec{\beta} \times \left\{ (\vec{H} \times \vec{E}) + (\vec{D} \times \vec{B}) \right\}$$

$= 0$, using (7) and (8).

Under transformation (6),

$$(\vec{E}' \times \vec{D}') + (\vec{H}' \times \vec{B}') = i\delta \vec{a} \times (\vec{E} \times \vec{H}) + i\delta \vec{a} \times (\vec{B} \times \vec{D}) + \delta \vec{a} \times (\vec{H} \times \vec{B}) + \delta \vec{a} \times (\vec{E} \times \vec{D})$$

$$= 0.$$

Finally, under transformation (6′),

$$(\vec{E}' \times \vec{D}') + (\vec{H}' \times \vec{B}') = 2i\delta \vec{\beta} (\vec{D}\vec{B} - \vec{E}\vec{H}) - i\delta \left\{ \vec{B} (\vec{D} \cdot \vec{\beta}) + \vec{D} (\vec{B} \cdot \vec{\beta}) \right\} + i\delta \left\{ \vec{H} (\vec{E} \cdot \vec{\beta}) + \vec{E} (\vec{H} \cdot \vec{\beta}) \right\} + 2\delta \vec{\beta} \times (\vec{E} \times \vec{D})$$

and the coefficients multiplying $\vec{\beta}$ scalarly and vectorially do not vanish. Remembering that $\vec{\beta}$ is an arbitrary vector with the " Kennzahlen " $\beta_1, \beta_2, \beta_3$ belonging to an arbitrary anti-dual antisymmetric $v_{ik}$, this shows that condition (8) is not invariant under the (C)-transformations.

*7. Lorentz-invariance of the field equations.*

Consider now the right-hand side of the first of the equations (3) and let us determine how it is transformed under (6).

$$\vec{D}'^2 = \vec{D}^2 + 2i\delta\vec{a}\,(\overrightarrow{H - iD} \times \vec{D}) = \vec{D}^2 + 2i\delta\vec{a}\,(\vec{H} \times \vec{D})$$

$$\vec{B}'^2 = \vec{B}^2 + 2i\delta\vec{a}\,(\overrightarrow{B - iE} \times \vec{B}) = \vec{B}^2 + 2i\delta\vec{a}\,(\vec{B} \times \vec{E})$$

$$(\vec{B}' \cdot \vec{D}') = (\vec{B} \cdot \vec{D}) + \delta\vec{a}\,(\overrightarrow{B - iE} \times \vec{D}) + i\delta\vec{a}\,(\overrightarrow{H - iD} \times \vec{B})$$

$$= (\vec{B} \cdot \vec{D}) - i\delta\vec{a}\,(\vec{E} \times \vec{D}) + i\delta\vec{a}\,(\vec{H} \times \vec{B})$$

*i.e.*, $R' = R + 2i\delta\vec{a}\,(\vec{H} \times \vec{B}) = R - 2i\delta\vec{a}\,(\vec{E} \times \vec{D})$ using (8)

$$\therefore \quad R'^2 = R^2 + 4i\delta R\vec{a}\,(\vec{H} \times \vec{B})$$

and $(1 + \vec{D}'^2)(1 + \vec{B}'^2) - R'^2 = \Omega + 2i\delta\,\Omega_2$ .. .. .. (9)

where $\Omega = (1 + \vec{D}^2)(1 + \vec{B}^2) - R^2$

and $\Omega_2 = (1 + \vec{B}^2)\,\vec{a} \cdot (\vec{H} \times \vec{D}) + (1 + \vec{D}^2)\,\vec{a} \cdot (\vec{B} \times \vec{E}) - 2R\vec{a}\,(\vec{H} \times \vec{B})$.

Similarly for the numerator,

$$\vec{D}'(1 + \vec{B}'^2) - \vec{B}'R' = \left\{\vec{D}(1 + \vec{B}^2) - \vec{B}R\right\} + \delta\vec{\Omega}_1 \quad .. \quad .. \quad (10)$$

where $\vec{\Omega}_1 = i(1 + \vec{B}^2)(\vec{a} \times \overrightarrow{H - iD}) + 2i\vec{D}\left\{\vec{a} \cdot (\vec{B} \times \vec{E})\right\}$

$$- 2i\vec{B}\left\{\vec{a} \cdot (\vec{H} \times \vec{B})\right\} - R(\vec{a} \times \overrightarrow{B - iE}).$$

Hence the expression

$$\frac{\vec{D}'(1 + \vec{B}'^2) - \vec{B}'R'}{\sqrt{(1 + \vec{D}'^2)(1 + \vec{B}'^2) - R'^2}} = \frac{\left\{\vec{D}(1 + \vec{B}^2) - \vec{B}R\right\} + \delta\vec{\Omega}_1}{\sqrt{\Omega + 2i\delta\Omega_2}}, \text{ from (9) and (10)}$$

$$= \frac{\left\{\vec{D}(1 + \vec{B}^2) - \vec{B}R\right\} + \delta\vec{\Omega}_1}{\sqrt{\Omega}} \left\{1 + \frac{2i\delta\Omega_2}{\Omega}\right\}^{-\frac{1}{2}}$$

$$= \frac{\left[\left\{\vec{D}(1 + \vec{B}^2) - \vec{B}R\right\} + \delta\vec{\Omega}_1\right]\left[1 - \frac{i\delta\Omega_2}{\Omega}\right]}{\sqrt{\Omega}}$$

$$= \frac{\vec{D}(1 + \vec{B}^2) - \vec{B}R}{\sqrt{\Omega}} + \frac{\delta\left\{\vec{\Omega}_1 - i\Omega_2\vec{E}/\sqrt{\Omega}\right\}}{\sqrt{\Omega}}, \text{ using (3)}$$

$$= \vec{E} + \frac{\delta\vec{\Omega}_1}{\sqrt{\Omega}} - \frac{i\delta\Omega_2\vec{E}}{\Omega} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11)$$

$$\text{Now, } \Omega_2 = \frac{2\,(1+\vec{B}^2)\,(1+\vec{D}^2)}{\sqrt{\Omega}}\,\vec{a}\,(\vec{B}\times\vec{D}) - 2R\vec{a}\left\{\frac{\vec{B}\,(1+\vec{D}^2)-\vec{D}R}{\sqrt{\Omega}}\times\vec{B}\right\}$$

[substituting for $\vec{H}$ and $\vec{E}$ from (3)]

$$= 2\sqrt{\Omega}\,\vec{a}\,(\vec{B}\times\vec{D}) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

$$\text{Also } \Omega_1 = \left\{(1+\vec{B}^2)\,(\vec{a}\times\vec{D}) - R\,(\vec{a}\times\vec{B})\right\} + i\,(1+\vec{B}^2)\,(\vec{a}\times\vec{H})$$
$$+ iR\,(\vec{a}\times\vec{E}) + 2i\vec{D}\left\{\vec{a}\,(\vec{B}\times\vec{E})\right\} - 2i\vec{B}\,\{\vec{a}\,(\vec{H}\times\vec{B})\}$$
$$= \sqrt{\Omega}\,(\vec{a}\times\vec{E}) + i\,(1+\vec{B}^2)\left\{\vec{a}\times\frac{\vec{B}\,(1+\vec{D}^2)-\vec{D}R}{\sqrt{\Omega}}\right\}$$
$$+ iR\left\{\vec{a}\times\frac{\vec{D}\,(1+\vec{B}^2)-\vec{B}R}{\sqrt{\Omega}}\right\}$$
$$+ 2i\vec{D}\left\{\vec{a}\,(\vec{B}\times\vec{E})\right\} + 2i\vec{B}\left\{\vec{a}\,(\vec{E}\times\vec{D})\right\}$$
$$= \sqrt{\Omega}\,(\vec{a}\times\vec{E}) + i\sqrt{\Omega}\,(\vec{a}\times\vec{B}) + 2i\vec{D}\,(\vec{a}\vec{B}\vec{E}) + 2i\vec{B}\,(\vec{a}\vec{E}\vec{D}) \quad .. \quad (13)$$

(the last two terms containing scalar triple products within brackets).

Putting (12) and (13) in (11) we get

$$\text{L. H. S. of (11)} = \vec{E} + \delta\,(\vec{a}\times\vec{E}) + i\delta\,(\vec{a}\times\vec{B})$$
$$+ \frac{2i\delta}{\sqrt{\Omega}}\left\{\vec{D}\,(\vec{a}\,\vec{B}\,\vec{E}) + \vec{B}\,(\vec{a}\,\vec{E}\,\vec{D}) - \vec{E}\,(\vec{a}\,\vec{B}\,\vec{D})\right\}.$$

Now for any four vectors $a, b, c, d$ we can deduce the identity

$$\vec{a}\,(\vec{b}\,\vec{c}\,\vec{d}) - \vec{b}\,(\vec{a}\,\vec{c}\,\vec{d}) + \vec{c}\,(\vec{a}\,\vec{b}\,\vec{d}) - \vec{d}\,(\vec{a}\,\vec{b}\,\vec{c}) = 0$$

and using this identity the terms within { } on the right hand side of the above expression reduce to

$$\vec{a}\,(\vec{D}\,\vec{B}\,\vec{E}) \text{ which is equal to}$$
$$= \vec{a}\,(\vec{B}\,\vec{E}\,\vec{D}) = \vec{a}\left\{\vec{B}\cdot(\vec{E}\times\vec{D})\right\} = \vec{a}\left\{\vec{B}\cdot(\vec{B}\times\vec{H})\right\}$$
$$= \vec{a}\left\{\vec{H}\cdot(\vec{B}\times\vec{B})\right\} = 0.$$

Hence,

$$\frac{\vec{D}'\,(1+\vec{B}'^2) - \vec{B}'R'}{\sqrt{(1+\vec{D}'^2)\,(1+\vec{B}'^2) - R'^2}} = \vec{E} + \delta\,(\vec{a}\times\vec{E}) + i\delta\,(\vec{a}\times\vec{B})$$
$$= \vec{E} + i\delta\,(\vec{a}\times\vec{B} - i\vec{E})$$
$$= \vec{E}' \quad .. \quad .. \quad .. \quad .. \quad (14)$$

[using (6)]

Hence we have proved the Lorentz-invariance of the first of the equations (3).

We can similarly prove the invariance of the second of the equations (3), considering $\dfrac{\vec{B}'(1+\vec{D}'^2)-\vec{D}'R'}{\sqrt{(1+\vec{D}'^2)(1+\vec{B}'^2)-R'^2}}$, the denominator is given by exactly the same expression (9). As regards the numerator we can write it in the form

$$\{\vec{B}(1+\vec{D}^2)-\vec{D}R\}+\delta\vec{\Omega}_3 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10')$$

where $\vec{\Omega}_3=(1+\vec{D}^2)(\vec{a}\times\overrightarrow{B-iE})-iR(\vec{a}\times\overrightarrow{H-iD})+2i\vec{B}(\vec{a}\vec{H}\vec{D})$
$-2i\vec{D}(\vec{a}\vec{H}\vec{B})$,

and in place of (11) we have the expression

$$\vec{H}+\frac{\delta\vec{\Omega}_3}{\sqrt{\Omega}}-\frac{i\delta\Omega_2\vec{H}}{\Omega} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11')$$

where $\Omega_2=2\sqrt{\Omega}(\vec{a}\vec{B}\vec{D})$ .. .. .. .. .. (12')

and $\vec{\Omega}_3=\{\vec{a}\times[(1+\vec{D}^2)\vec{B}-\vec{D}R]\}-i(1+\vec{D}^2)(\vec{a}\times\vec{E})-iR(\vec{a}\times\vec{H})$
$+2i\vec{B}(\vec{a}\vec{H}\vec{B})-2i\vec{D}(\vec{a}\vec{H}\vec{B})$

$$=\sqrt{\Omega}(\vec{a}\times\vec{H})-i(1+\vec{D}^2)\left\{\vec{a}\times\frac{\vec{D}(1+\vec{B}^2)-\vec{B}R}{\sqrt{\Omega}}\right\}$$
$$-iR\left\{a\times\frac{\vec{B}(1+\vec{D}^2)-\vec{D}R}{\sqrt{\Omega}}\right\}+2i\vec{B}(\vec{a}\vec{H}\vec{B})-2i\vec{D}(\vec{a}\vec{H}\vec{B}).$$

$$=\sqrt{\Omega}(\vec{a}\times\vec{H})-i\sqrt{\Omega}(\vec{a}\times\vec{D})+2i\vec{B}(\vec{a}\vec{H}\vec{B})-2i\vec{D}(\vec{a}\vec{H}\vec{B}).. \quad (13')$$

$\therefore$ (11′) reduces to

$$\vec{H}+\delta(\vec{a}\times\vec{H})-i\delta(\vec{a}\times\vec{D})+\frac{2i\delta}{\sqrt{\Omega}}\left\{\vec{B}(\vec{a}\vec{H}\vec{D})-\vec{D}(\vec{a}\vec{H}\vec{B})-\vec{H}(\vec{a}\vec{B}\vec{D})\right\}$$

From the identity of triple scalar products mentioned above the last term within the { } reduces to

$$\vec{a}(\vec{B}\vec{H}\vec{D})$$
$$=\vec{a}(\vec{D}\vec{B}\vec{H})=\vec{a}(\vec{D}\vec{E}\vec{D}), \text{ using (8)}$$
$$=0.$$

Hence we have shown that

$$\frac{\vec{B}'(1+\vec{D}'^2)-\vec{D}'R'}{\sqrt{(1+\vec{D}'^2)(1+\vec{B}'^2)-R'^2}}=\vec{H}+\delta(\vec{a}\times\vec{H})-i\delta(\vec{a}\times\vec{D})$$
$$=\vec{H}+\delta(\vec{a}\times\overrightarrow{H-iD})$$
$$=\vec{H}', \text{ using (16)}$$

which proves the Lorentz-invariance of the second of the equations (3).

*8. Equations when $\vec{E}$ and $\vec{H}$ are independent variables.*[7]

Starting from the Lagrangian

$$L = \sqrt{1 + (\vec{B}^2 - \vec{E}^2) - G^2} - 1 \quad .. \quad .. \quad .. \quad (a)$$

where $G = (\vec{E} \cdot \vec{B})$ .. .. .. .. .. (*b*)

we want to express the function

$$V = L - (\vec{B}\vec{H}) \quad .. \quad .. \quad .. \quad .. \quad (c)$$

as function of $\vec{E}$ and $\vec{H}$.

From the equations derived from L, we have

$$\vec{H} = \frac{\partial L}{\partial \vec{B}} = \frac{\vec{B} - G\vec{E}}{\sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2}} \quad .. \quad .. \quad .. \quad (d)$$

therefore

$$(\vec{B} \cdot \vec{H}) = \frac{\vec{B}^2 - G^2}{\sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2}}$$

and from (*c*) using (*a*)

$$V = \sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2} - \frac{\vec{B}^2 - G^2}{\sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2}} - 1$$

$$V = \frac{1 - \vec{E}^2}{\sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2}} - 1 \quad .. \quad .. \quad .. \quad (e)$$

We now denote

$$S = (\vec{E} \cdot \vec{H}) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (f)$$

and obtain for S from (*d*)

$$S = \frac{G\,(1 - \vec{E}^2)}{\sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2}} \quad .. \quad .. \quad .. \quad (g)$$

From (*g*) and (*e*) it follows

$$V = \frac{S}{G} - 1 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (h)$$

Now we have only to express G in terms of $\vec{E}$ and $\vec{H}$. For this purpose we

[7] In this paragraph, we have followed exactly the same method as in the appendix, due to P. Weiss in Born-Infeld, Ref. (1), p. 544.

write first $(d)$ in the following form

$$\vec{H} = \frac{\vec{B} - G\vec{E}}{1 - \vec{E}^2} \cdot \frac{1 - \vec{E}^2}{\sqrt{1 + \vec{B}^2 - \vec{E}^2 - G^2}}$$

and because of $(g)$

$$\vec{H} = \frac{\vec{B} - G\vec{E}}{1 - \vec{E}^2} \cdot \frac{S}{G} \quad .. \quad .. \quad .. \quad .. \quad (i)$$

Now we solve $(g)$ and $(i)$ with respect to G by eliminating $\vec{B}$.

Squaring $(g)$ gives

$$-S^2\vec{B}^2 + G^2\{S^2 + (1 - \vec{E}^2)^2\} = S^2(1 - \vec{E}^2) \quad .. \quad (j)$$

Squaring $(i)$ gives

$$S^2\vec{B}^2 = G^2\{\vec{H}^2(1 - \vec{E}^2)^2 + S^2(2 - \vec{E}^2)\} \quad .. \quad .. \quad (k)$$

From $(j)$ and $(k)$ follows

$$G^2\{(1 - \vec{E}^2)^2(1 - \vec{H}^2) - S^2(1 - \vec{E}^2)\} = S^2(1 - \vec{E}^2)$$

or,

$$G = \frac{S}{\sqrt{(1 - \vec{E}^2)(1 - \vec{H}^2) - S^2}} \quad .. \quad .. \quad .. \quad (l)$$

Introduction of $(l)$ into $(h)$ gives

$$V = \sqrt{(1 - \vec{E}^2)(1 - \vec{H}^2) - S^2} - 1 \quad .. \quad .. \quad (m)$$

As regards the equations to be derived from V, we have

$$dV = dL - \vec{B}d\vec{H} - \vec{H}d\vec{B}$$

and
$$dL = \frac{\partial L}{\partial \vec{E}} d\vec{E} + \frac{\partial L}{\partial \vec{B}} d\vec{B}$$

$$= -\vec{D}d\vec{E} + \vec{H}d\vec{B}$$

$$\therefore dV = -\vec{D}d\vec{E} + \vec{H}d\vec{B} - \vec{B}d\vec{H} - \vec{H}d\vec{B}$$

$$= -\vec{D}d\vec{E} - \vec{B}d\vec{H}$$

$$\therefore \vec{D} = -\frac{\partial V}{\partial \vec{E}}; \quad \vec{B} = -\frac{\partial V}{\partial \vec{H}} \quad .. \quad .. \quad .. \quad .. \quad (15)$$

Using for V the expression obtained in (*m*) above, these can be written as

$$\left.\begin{aligned}\vec{D} &= \frac{(1-\vec{H}^2)\,\vec{E}+S\vec{H}}{\sqrt{(1-\vec{E}^2)\,(1-\vec{H}^2)-S^2}}\\ \vec{B} &= \frac{(1-\vec{E}^2)\,\vec{H}+S\vec{E}}{\sqrt{(1-\vec{E}^2)\,(1-\vec{H}^2)-S^2}}\end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad (16)$$

*9. Lorentz-invariance of the field equations derived from V.*

We now proceed to prove that the equations (16) are invariant with respect to the (C)-transformations contained in (6′).

We write

$$\vec{E}'^2 = \vec{E}^2 - 2i\delta\vec{E}\,(\vec{\beta}\times\overrightarrow{B+iE}) = \vec{E}^2 - 2i\delta\vec{E}\,(\beta\times\vec{B}) = \vec{E}^2 - 2i\delta\vec{\beta}\,(\vec{B}\times\vec{E})$$

$$\vec{H}'^2 = \vec{H}^2 + 2\delta\vec{H}\,(\vec{\beta}\times\overrightarrow{H+iD}) = \vec{H}^2 + 2i\delta\vec{H}\,(\beta\times\vec{D}) = \vec{H}^2 - 2i\delta\vec{\beta}\,(\vec{H}\times\vec{D})$$

$$\begin{aligned}S' = (\vec{E}'\cdot\vec{H}') &= S + \delta\vec{E}\,(\vec{\beta}\times\overrightarrow{H+iD}) - i\delta\vec{H}\,(\vec{\beta}\times\overrightarrow{B+iE})\\ &= S + i\delta\vec{E}\,(\vec{\beta}\times\vec{D}) - i\delta\vec{H}\,(\vec{\beta}\times\vec{B}) = S - i\delta\vec{\beta}\,(\vec{E}\times\vec{D})\\ &\qquad + i\delta\vec{\beta}\,(\vec{H}\times\vec{B})\\ &= S + 2i\delta\vec{\beta}\,(\vec{H}\times\vec{B}).\end{aligned}$$

$$S'^2 = S^2 + 4i\delta S\vec{\beta}\,(\vec{H}\times\vec{B})$$

$$\therefore\quad (1-\vec{E}'^2)\,(1-\vec{H}'^2) - S'^2 = \Omega + 2i\delta\Omega_2$$

where $\quad \Omega = (1-\vec{E}^2)\,(1-\vec{H}^2) - S^2$

and $\quad \Omega_2 = (1-\vec{E}^2)\,\vec{\beta}\,(\vec{H}\times\vec{D}) + (1-\vec{H}^2)\,\vec{\beta}\,(\vec{B}\times\vec{E}) - 2S\vec{\beta}\,(\vec{H}\times\vec{B}).$

Similarly $\vec{E}'\,(1-\vec{H}'^2) + \vec{H}'S' = \{\vec{E}\,(1-\vec{H}^2) + \vec{H}\,S\} + \delta\vec{\Omega}_1$, where

$$\vec{\Omega}_1 = 2i\vec{E}\,(\vec{\beta}\vec{H}\vec{D}) - i\,(1-\vec{H}^2)\,(\vec{\beta}\times\overrightarrow{B+iE}) + 2i\vec{H}\,(\vec{\beta}\vec{H}\vec{B})$$
$$+ S\,(\vec{\beta}\times\overrightarrow{H+iD}).$$

Hence the right-hand side of the first equation in (16) in the co-ordinate

system $\Sigma'$ reduces to

$$\frac{\{\vec{E}\,(1-\vec{H}^2)+\vec{H}\vec{S}\}+\delta\vec{\Omega}_1}{\sqrt{\Omega}+2i\delta\Omega_2}=\vec{D}+\frac{\delta\vec{\Omega}_1}{\sqrt{\Omega}}-\frac{i\delta\Omega_2\vec{D}}{\Omega},\ \text{just as (11).}$$

Corresponding to (12) and (13), $\Omega_2$ and $\vec{\Omega}_1$ simplify to

$$\Omega_2=2\sqrt{\Omega}\,\vec{\beta}\,(\vec{H}\times\vec{E})$$

and $\vec{\Omega}_1=\sqrt{\Omega}\,(\vec{\beta}\times\vec{D})-i\sqrt{\Omega}\,(\vec{\beta}\times\vec{H})+2i\vec{E}\,(\vec{\beta}\vec{H}\vec{D})+2i\vec{H}\,(\vec{\beta}\vec{H}\vec{B})$.

Hence

$$\frac{\vec{E}'\,(1-\vec{H}'^2)+\vec{H}'\vec{S}'}{\sqrt{(1-\vec{E}'^2)\,(1-\vec{H}'^2)-S'^2}}=\vec{D}+\delta\,(\vec{\beta}\times\vec{D})-i\delta\,(\vec{\beta}\times\vec{H})$$

$$+\frac{2i\delta}{\sqrt{\Omega}}\left[\vec{H}\,(\vec{\beta}\vec{H}\vec{B})+\vec{E}\,(\vec{\beta}\vec{H}\vec{D})-\vec{D}\,(\vec{\beta}\vec{H}\vec{E})\right]$$

$$=\vec{D}+\delta\,(\vec{\beta}\times\vec{D})-i\delta\,(\vec{\beta}\times\vec{H})+\frac{2i\delta}{\sqrt{\Omega}}\left\{\vec{\beta}\,(\vec{E}\vec{H}\vec{D})\right\}$$

[using (8) and the vector-identity],

$$=\vec{D}-i\delta\,(\vec{\beta}\times\overrightarrow{H+iD}),\ \text{since}\ (\vec{E}\vec{H}\vec{D})=(\vec{H}\vec{D}\vec{E})$$

$$=(\vec{H}\vec{H}\vec{B})\ \text{from (8)}=0.$$

$$=\vec{D}',\ \text{using (6')}.$$

This proves the Lorentz-invariance of the first equation of (16).

For the second equation, we need only calculate $\vec{\Omega}_3$ corresponding to (13'). This is easily found to be

$$\vec{\Omega}_3=\sqrt{\Omega}\,(\vec{\beta}\times\vec{B})+i\sqrt{\Omega}\,(\vec{\beta}\times\vec{E})+2i\vec{H}\,(\vec{\beta}\vec{B}\vec{E})+2i\vec{E}\,(\vec{\beta}\vec{H}\vec{B})$$

and we find, as in the previous case,

$$\frac{(1-\vec{E}'^2)\,\vec{H}'+\vec{E}'\vec{S}'}{\sqrt{(1-\vec{E}'^2)\,(1-\vec{H}'^2)-S'^2}}=\vec{B}+\delta\,(\vec{\beta}\times\vec{B})+i\delta\,(\vec{\beta}\times\vec{E})$$

$$=\vec{B}+\delta\,(\vec{\beta}\times\overrightarrow{B+iE})$$

$$=\vec{B}',$$

proving the invariance of the second of the equations (16).

### *10. Conclusion.*

We have proved the Lorentz-invariance of the equations connecting the primary and secondary vectors in the cases where the action functions are U and V, and the Lorentz-invariance of the field equations derived U and V follows as an immediate consequence.

I wish to thank Prof. Born for proposing the problem and suggesting that I should use the Einstein-Mayer semi-vector theory for proving the Lorentz-invariance of the equations concerned.

# THE ACID CONTENT OF SOME OF OUR VEGETABLE FOODSTUFFS.

## Part II. Amchur or *Mangifera Indica*.

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and
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"Men and animals must ingest considerable quantities of compounds like citric, malic, tartaric and oxalic acids. Yet the dietary function of these organic acids of vegetables is almost entirely unknown. How do they function in alimentation? Do they find their way into the systematic circulation or are they disposed of in the liver?"[1] Whatever answer future research may make to this query of Professor Mendel, it is true that in India, more than anywhere else, a very large variety of vegetables and vegetable products is known, and extensively used, for their acid contents. Sometimes raw, sometimes cooked, these are used, throughout the length and breadth of the country, for flavouring dals, curries, vegetables, condiments, pickles, achars and even drinks. Tradition has handed down a mass of information regarding the suitability and the precise uses in diet of every one of these, while the Ayurvedic and the Unani physicians have even a more crystallised knowledge of the peculiar advantages and the specific dangers attending the use and abuse of each, either as an article of diet or of medicine. In addition to this knowledge, there are other factors to regulate their use, the chief of which are the economic, the geographic and the climatic conditions. These acid foods have scarcely received due attention, as a class, however, at the hands of the chemists, analytical and physiological alike. It is to be hoped that, at a time when nutrition itself is attracting a new and world-wide attention, these invariable articles of our daily food will not have long to wait.

Of a few members of this class, a considerable analytical knowledge does undoubtedly exist. The *Citrus* family is an example in point. In health as well as in disease, members of this family have been considered, in India particularly, as of first rate importance. The discovery of their vitamin and mineral contents has lately pushed them into the forefront in the dietary of the civilised

world and has also thrown an interesting light on their dietetic value ; but this should not succeed in throwing in the background the more ancient and the more deeply human interest of their acid contents. Though analytical figures of the acids contained are available in literature, a fresh survey of the acid contents of those varieties popularly used would undoubtedly be useful.

The next in importance, perhaps, is tamarind, *Tamarindus Indica.* While the stone or the seed is not without use, the dried fruit, often salted and preserved for the year, finds its way into ever so many foods, drinks and even medicines, particularly in the south and southwest of India. The acid is reported to be mainly tartaric and investigations have also been made to utilise tamarind for the industrial production of tartaric acid, tartrates and alcohol,[2] though no commercial application is so far known.

The place of tamarind is taken, in many homes and in several provinces, by two species of *Garcinia* or by raw dried mango.

Of the *Garcinia,* the lesser known *Garcinia Cambogia* goes also by the nickname of *Vilayati Imli,* and its dried fruits, after the removal of the stone, are used very much like those of tamarind, particularly in the south, in Travancore, in Cochin and in South Malabar. " It is also used as a condiment and eaten with fish as a substitute for tamarind."[3] Like tamarind, it is found also to contain mainly tartaric acid and in about the same proportion, *viz.,* 10%.[4]

*Garcinia Indica,* better known as Kokam, is a much more popular stuff. Its acid contents are under investigation in this Laboratory.

The United Provinces know nought of Kokam and employ as a souring element the raw dried mango fruit, which is locally known as amchur [or mango-powder], or as Khatai, the generic term for all sourness. After the removal of the stone the raw mangoes are cut into slices and dried in the sun, and these find their way into markets and homes, as they can then keep for a year or more. A reference, very kindly supplied by Lt.-Col. R. N. Chopra from *Die Pflanzen-stoffe* by C. Wehmer (2nd Edition, Vol. I, 1929, Vol. II, 1931), says that the acid variety of *Mangifera Indica* contains the acid citric. Beyond this we have been unable to find any reference to the investigation of its acid contents.

The samples investigated by us were obtained from the local market. Three organic acids, tartaric, citric and oxalic, have been found in the amchur, in proportions of 6, 4 and 1% approximately. The ash was rather low, about 5%, and showed the presence of phosphates in addition to that of aluminium, iron, calcium, magnesium, sodium and potassium. The total acidity,

found by direct titration against alkali and calculated in terms of tartaric acid, was as high as about 15%. The presence was also detected of starch and glucose or glucosides.

*Experimental.*

*Moisture.*—The amchur, though sun-dried, still contained appreciable amounts of water. Weighed amounts were kept in an air-oven, at a little above 100° C., and the loss determined till the last weight was constant. Two samples gave respectively 14·73 and 14·75%, or 14·74% as the average moisture content.

*Ash.*—The ash obtained on incineration was, on an average in two experiments, 5·44%. A qualitative macro-analysis of the ash indicated phosphate, iron, aluminium, calcium, magnesium, sodium and potassium.

*Solubility.*—The amchur dried at 100° C. was found to contain about 13·65% of water-soluble material. For the purpose of extracting the organic acids, trial-extractions were made with a number of solvents, such as water, acetone, alcohol, ether and ethyl acetate. Water was undoubtedly a very suitable solvent, but on account of the presence of starch in the material, became very difficult to work with, as extractions with boiling water gave a pasty mass which could not be easily and quickly filtered. Acidified alcohol was found to be able to avoid the difficulty.

*Organic acids.*—The method finally adopted was as under. 100 g. of the powdered amchur were refluxed with 250 c.c. of ethyl alcohol (rectified about 92–95%), acidified with 10 c.c. of 2N hydrochloric acid. After a few hours, the solvent was removed and the amchur was refluxed with another lot of unacidified alcohol. This was repeated four or five times, till the extract ceased to give an acid reaction. From the accumulated extracts, alcohol was removed by distillation and the residue was treated with sufficient water. This was heated on the water-bath till all the alcohol was evaporated off, when the watery extract, coloured though clear, was treated with lead acetate solution. After the precipitated lead salts were removed, the filtrate was treated with basic lead acetate solution to ensure complete precipitation of the acids. The two precipitates were mixed and the filtrate was kept aside. The residue left after the amchur was exhaustively extracted with alcohol, was also kept for further observations.

The combined lead precipitates were washed with 50% alcohol and then treated with ammonia. The bulk of the precipitate dissolved and passed into the filtrate, leaving only a small residue. The filtrate must contain tartaric, citric and malic acids, and the residue may contain oxalic.[5] This residue was suspended in water and decomposed by hydrogen sulphide and

filtered. The filtrate on evaporation gave an acid liquid, which, in the presence of dilute sulphuric acid, reduced potassium permanganate solution in the warm. From a neutral solution of the syrup, calcium chloride solution gave a white precipitate of calcium oxalate, insoluble in acetic acid, which confirmed oxalic acid.

The filtrate of the ammonium salts, on treatment as described (5, *loc. cit.*), free from lead sulphide, was concentrated; aqueous potassium acetate solution, 95% alcohol and vigorous stirring helped to bring down a sticky precipitate of cream of tartar, which settled on keeping. The solution was poured off, and the precipitate was washed with diluted alcohol (2 parts alcohol and one of water), dissolved in acetic acid, and treated with lead acetate solution. From the precipitated lead salt, the free tartaric acid was separated in the usual way in aqueous solution, which on evaporation gave a syrup, and from the syrup, white crystals. The purified crystals melted at 169° C., alone as well as when mixed with some pure tartaric acid.

It weighed about 1·5 g., and its identity was further confirmed by other tests: such as charring on heating, reduction of ammoniacal silver nitrate solution, the Fenton's test, Mohler's test[6] and Pinerua's test,[7] all of which were found, by trials with the known organic vegetable acids, to be perfectly reliable for tartaric acid.

The liquid separated from the cream of tartar above, was treated with calcium chloride, ammonia and some alcohol. The precipitate formed might be the calcium salts of malic and citric acids: it was washed with hot lime water, whereby the malate would go in solution and the citrate would remain undissolved.

The filtrate was examined for malic acid. Sulphuric acid was added, the precipitated calcium sulphate filtered off, and lead acetate solution added. As it gave no precipitate, malic acid could not be present.

The residue of calcium citrate was treated with a calculated quantity of dilute sulphuric acid and the precipitated calcium sulphate removed by filtration. By means of lead acetate and hydrogen sulphide, the citric acid was again obtained in aqueous solution, which was evaporated to a thick syrup, cooled, kept in a vacuum desiccator for some days, and ultimately evaporated gently, to dryness on a water-bath, when white glistening plates, weighing about one gram, were obtained. It melted at 152° C. (anhydrous citric acid melts at 153° C.). Its identity was further confirmed by its behaviour on heating when it did not char but gave the pungent fumes of aconitic acid; by giving no precipitate in the cold from a neutral solution by the addition of calcium chloride solution, though it appeared immediately on boiling; and by answering Denigès' test.[8]

*Glucose.*—The filtrate left after the removal of the lead salts of the organic acids above, obtained by the first treatment with lead acetate and basic lead acetate solutions, was treated with hydrogen sulphide to remove lead completely, the precipitated lead sulphide was filtered off and the residual liquid was evaporated on a water-bath to a syrup, which gave out no crystals. The syrup indicated carbon, hydrogen and some inorganic materials. It reduced, however, Fehling's solution, reduced copper acetate in dilute acetic acid solution and gave Molisch's reaction for carbohydrates. The syrup was dissolved in water, treated with lead acetate solution, boiled and then ammonium hydroxide was cautiously added till a slight permanent precipitate was formed. On boiling, the salmon-red coloured precipitate, characteristic of glucose, was observed. This was filtered, washed and decomposed by hydrogen sulphide. After the removal of lead sulphide, the filtrate was concentrated and an osazone was prepared from it, which melted at 205° C. (glucosazone melts at 205° C.), and its melting-point was not changed when a mixed melting-point was taken with a known specimen of the glucosazone.

*Starch.*—The residue of the amchur left after the alcoholic extraction of amchur, and weighing, when air-dried, about 70 g., was refluxed with water for about four hours and filtered. This watery extract gave a blue colour on the addition of iodine solution, the colour disappearing on heating and re-appearing on cooling. An equal bulk of alcohol was added, which gave a colourless jelly. After filtering this off, the filtrate gave no colour with iodine solution, while the residue on the filter did as before. Neither the filtrate nor the jelly gave indications of proteins or of alkaloids, though the former showed potassium. The jelly was dried and powdered when it resembled, in appearance as well as in behaviour, starch. It was a white amorphous powder, which, on heating, decomposed, charred and emitted the smell of burning flour. Insoluble in cold water, it dissolved on boiling and did not immediately separate on cooling. This solution gave, besides the starch-iodide test, a white precipitate with lead acetate solution.

*Quantitative determinations of the organic acids: Tartaric Acid.*—10 g. of amchur were refluxed with 92–95 % alcohol repeatedly, till all the acids were extracted. This was very carefully filtered, and to the filtrate potassium acetate solution was added. It was vigorously stirred and left for settling overnight. The potassium hydrogen tartrate formed was both sticky and coloured. Instead, therefore, of weighing it directly as usual, it was, after washing, suspended in water and titrated directly against standard NaOH solution. (Trial experiments with pure potassium hydrogen tartrate similarly suspended in water and titrated had given accurate results.) The amount of

tartaric acid found was, in two similar determinations, 6·087% and 6·112% respectively.

*Determination of citric and oxalic acids.*—The filtrate obtained from the potassium hydrogen tartrate was treated with lead acetate till complete precipitation was effected. It was warmed and the lead salts filtered off. Treatment of this precipitate with ammonia left the lead oxalate undissolved. The latter was removed from the dissolved lead citrate and thoroughly washed.

The insoluble lead oxalate was suspended in water, decomposed by hydrogen sulphide, the lead sulphide separated, and the filtrate and washings evaporated till $H_2S$ was completely removed. The amount of oxalic acid in this was determined by titration against standard potassiuum permanganate solution. The oxalic acid found in two samples was 1·076 % and 1·074 % respectively.

The combined filtrate and washings containing the citrate were acidified with acetic acid and the acid was precipitated as the lead salt. This precipitate was filtered off, treated with $H_2S$, while suspended in water, the lead sulphide removed and washed, and the filtrate and the washings containing the free citric acid were titrated against standard sodium hydroxide. The citric acid in two determinations was found : 4·218% and 4·236%.

*Determination of glucose.*—The amchur solution was clarified by a preliminary treatment with basic lead acetate solution which brought down the acids and some other impurities. After the removal of these, the remaining filtrate and washings were treated with oxalic acid to remove the excess of lead. In the remaining solution, the glucose was determined by the method of Lane and Eynon, using methylene blue as an internal indicator.[9] Two experiments gave the amount of glucose as 2·9895% and 3·0135% respectively.

*Summary.*

| The mean of two concordant determinations :— | % |
|---|---|
| Water in sun-dried amchur .. .. .. | 14·74 |
| Water-soluble, in 100° C. dried sample .. .. | 13·65 |
| Total acidity, as tartaric acid .. .. .. | 15·215 |
| Tartaric acid .. .. .. .. | 6·099 |
| Citric acid .. .. .. .. | 4·227 |
| Oxalic acid .. .. .. .. | 1·075 |
| Glucose .. .. .. .. .. | 3·0015 |
| Ash .. .. .. .. .. | 5·44. |

REFERENCES.

1. Dr. Lafayette B. Mendel (Sterling Professor of Physiological Chemistry, Yale University), *Science*, 1933, **78**, 317.
2. Woy, *Chemisches Central-Blatt*, 1905, **2**, 1042; Sudborough and Vridhachalam, *Jour. Inst. Sci.*, 1920, **3**, 61; Bathum and Nigam, *Bull. Agri. Reser. Inst., Pusa*, 1924, No. 153; Marsden, *Jour. Ind. Inst. Sci.*, 1923, **5**, 157.
3. Watt, *Commercial Products of India*, 1908, 552.
4. Kuriyan and Pandya, *Jour. Ind. Chem. Soc.*, 1931, **8**, 469.
5. The procedure followed is the Fleischer's process, as detailed in *The Chemical Investigation of Plants*, by Rosenthaler and Ghosh, Edition 1930, p. 120 onwards.
6. Rosenthaler and Ghosh, as above, p. 124; *Bull. Soc. Chim.*, Paris, 1890, 3, **4**, 728.
7. Pinerua, *Compt. Rend.*, **124**, 291; Mulliken, *Identification of Organic Compounds*, 1914, **1**, 83.
8. *Jour. pharm. chim.*, 1898, **7** (6), 487; *Organic Chemical Analysis*, by Thorpe and Whiteley, 1925, p. 81.
9. Lane and Eynon, *Jour. Soc. Chem. Indus.*, 1923, **43**, 32T; *ibid.*, 1925, **44**, 150T.

# AN OPTICAL INVESTIGATION OF SOME INDIAN OILS.

## II. Raman Effect.

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### 1. *Introduction.*

In a previous paper (Jogarao, 1936)[1] forming the first of this series, the refractive indices and the depolarisation factors of five vegetable oils have been measured. Olive and gingelli oils showed a low value for the depolarisation while castor, cocoanut and groundnut oils showed comparatively high values. In this paper the results obtained from an observation of the Raman spectra of these five oils are given. In addition, cocogem and ghee also have been examined.

The oils obtained in the market have been subjected to the same process of purification and refining detailed in the previous paper and thus rendered suitable for optical investigation. Cocogem obtained in the market in vacuum-sealed tins has been directly transferred into the tube and examined as such. The ghee employed is buffalo ghee, and has been subjected to the same process of purification.

### 2. *Experimental Arrangements.*

The oil under examination is contained in an ordinary Wood's tube. Light from a six inch quartz mercury arc has been condensed on to it by means of a large glass condenser. The Raman spectra are photographed on Golden Iso-zenith plates with a Hilger Constant Deviation spectrograph. An exposure of nearly 48 hours has been given in each case. In order to definitely fix the assignment of the Raman lines observed, two different pictures, one with full light and the other with a filter of strong quinine sulphate solution interposed in the path of the incident light, have been obtained with each one of the oils. The filter is contained in a rectangular cell one centimetre thick. This filter, by completely absorbing the 4046 radiation, helps to diminish the fluorescence. In spite of this precaution much continuous spectrum has been obtained in the spectrograms. For pictures without filter, an exposure of about 18 hours was found to be sufficient. It may

be noticed here that on account of the continuous spectrum, some of the Raman lines may not have been detected. Those recorded could only be located and measured with some difficulty.

*3. Results.*

TABLE I. *Groundnut oil.*

| λ Raman line | $\nu$ | Exciting line | $\Delta\nu$ | Intensity |
|---|---|---|---|---|
| 4969·7 | 20116 | 22938 | 2822 | 2*b* |
| 4571·4 | 21869 | 24705 | 2836 | 2*b* |

$\Delta\nu$ : 2829 (2*b*)

TABLE II. *Cocoanut oil.*

| λ Raman line | $\nu$ | Exciting line | $\Delta\nu$ | Intensity |
|---|---|---|---|---|
| 4992·0 | 20026 | 22938 | 2912 | 3*b* |
| 4653·4 | 21484 | ,, | 1454 | 2 |
| 4625·4 | 21614 | ,, | 1324 | 1 |

$\Delta\nu$ : 1324 (1), 1454 (2), 2912 (3*b*).

TABLE III. *Gingelli oil.*

| λ Raman line | $\nu$ | Exciting line | $\Delta\nu$ | Intensity |
|---|---|---|---|---|
| 4982·7 | 20064 | 22938 | 2874 | 2*b* |
| 4698·7 | 21277 | ,, | 1661 | 2 |
| 4656·5 | 21469 | ,, | 1469 | 3 |
| 4622·3 | 21626 | ,, | 1302 | 1 |
| 4578·8 | 21834 | 24705 | 2871 | 2*b* |

$\Delta\nu$ : 1302 (1), 1469 (3), 1661 (2), 2873 (2*b*).

TABLE IV. *Ghee.*

| λ Raman line | $\nu$ | Exciting line | $\Delta\nu$ | Intensity |
|---|---|---|---|---|
| 4991·9 | 20027 | 22938 | 2911 | 3*b* |
| 4650·0 | 21499 | ,, | 1439 | 3 |
| 4623·3 | 21623 | ,, | 1315 | 1 |
| 4583·9 | 21809 | 24705 | 2896 | 2*b* |

$\Delta\nu$: 1315 (1), 1439 (3), 2904 (3*b*).

In the case of castor and olive oils and cocogem, the continuous spectrum is very intense and no lines or bands could be observed at all.

*4. Discussion of Results.*

The Raman frequencies obtained in the case of various oils are collected together in Table V.

TABLE V.

| Oil | Raman Frequencies. | | | |
|---|---|---|---|---|
| Groundnut oil .. | .... | .... | .... | 2829 |
| Cocoanut oil .. .. | 1324 | 1454 | .... | 2912 |
| Gingelli oil .. .. | 1302 | 1469 | 1661 | 2873 |
| Ghee .. .. | 1315 | 1439 | .... | 2904 |

It may be noted that all the oils for which Raman lines have been recorded exhibit the usual aliphatic C–H frequency at about 2900. Besides this high frequency, gingelli oil, cocoanut oil and ghee exhibit frequencies at about 1450 which may be ascribed to a transverse oscillation of the same group. There is a frequency at 1300 in all these oils which may presumably be attributed to the C–O–C group.

From the point of view of the molecular structure of the chief constituents of these oils, the appearance of a Raman line at 1660 in gingelli oil is of great significance. It is well known that this frequency indicates the presence of a C = C group. The fact that the chief constituent of gingelli oil (Paranjpe and Deshpande, 1935)[2] is a Triolein, *i.e.*, a glyceride of oleic acid and therefore

possesses C = C groups, is in excellent agreement with the above observation. Similar results should be expected in olive oil and castor oil also but the strong continuous spectrum has presumably masked the Raman lines altogether.

The cocoanut oil stands on a different footing in that its chief constituent is a Trilaurin (Paranjpe and Deshpande, 1935),[2] *i.e.*, a glyceride of lauric acid. The latter is a saturated acid and therefore no C = C groups are present in the chief constituent of cocoanut oil. Accordingly no line is observed in the region of 1650.

The case of ghee is interesting as in the present investigation no line which may be attributed to C = C has been recorded. Two different formulæ have been suggested for the principal constituent of butter (Lewkowitsch, 1922),[3] namely,

$$C_3H_5 \begin{cases} OC_4H_7O \\ OC_{16}H_{31}O \\ OC_{18}H_{33}O \end{cases}$$

and

$$C_3H_5 \begin{cases} OC_4H_7O \\ OC_{16}H_{31}O \\ OC_{18}H_{35}O \end{cases}$$

The former includes a C = C group whereas the latter is saturated. The results of the present investigation thus support the latter formula.

The author wishes to express his gratefulness to Mr. S. Bhagavantam, the Head of the Physics Department, for his kind and valuable guidance during the course of this work.

REFERENCES.

1. Jogarao, Ch. V., *Proc. Ind. Acad. Sci.*, 1936, **4**, 327.
2. Paranjpe and Deshpande, *Proc. Ind. Acad. Sci.*, 1935, **3**, 880.
3. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats and Waxes*, 1922, Vol. 2, p. 824.

# THE RELATIVE EFFICIENCIES OF THE MULTISTAGE AND ONE STAGE PROCESS IN THE ELECTROLYTIC PREPARATION OF HEAVY WATER.

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§ 1. It has been observed by Washburn[1] that $\alpha'$ the measure of the efficiency of separation, in the electrolytic preparation of heavy water, carried under the same conditions as are existent in the working of a commercial cell tends to assume small values. This decrease in $\alpha'$ can be ascribed to a number of factors.[3] We are concerned here only with one of these, namely, the effect of the 'continual', *i.e.*, instalmentwise or multistage addition of 'fresh-water'. The vitiating influence of this on $\alpha'$ has been recognised as early as 1932 by Washburn.[2] It is shown that $\delta$ the relative magnitude of the step, *i.e.*, the fractional amount of fresh-water added is an important determinant. It is proposed in the following to give a quantitative estimate of the decrease in $\alpha'$ as a function of $\delta$, etc. for *the low heavy water concentration stage*, taking as the basis, the formula given by Urey[2] connecting the initial and final heavy water contents with the corresponding volumes of water in the electrolytic process.

§ 2. Urey[3] has shown from considerations put forward by Lord Rayleigh, for the fractional distillation of two liquids, that

$$\left(\frac{1-N}{1-N_0}\right)^{1/\alpha'-1}\left(\frac{N}{N_0}\right)^{\alpha'/\alpha'-1}=\frac{V_0}{V} \quad .. \quad .. \quad .. \quad (1)$$

where

$N_0$ = initial mol fraction of heavy water in the mixture.

$N$ = final mol fraction of heavy water in the mixture.

$V_0$ = initial volume of the mixture (before electrolysis).

$V$ = final volume of the mixture (after electrolysis).

$\alpha'$ = separation factor.

By mol fraction of heavy water is here meant the fraction,

$$\frac{\text{No. of mols of heavy water}}{\text{No. of mols of (heavy water + ordinary water)}}.$$

For low values of N and $N_0$ we can write with sufficient accuracy

$$\left(\frac{N}{N_0}\right)^{\alpha'/\alpha'-1} = \frac{V_0}{V} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

It is easily shown that if we mix a volume $V_1$ of mol fraction $N_1$ with volume $V_2$ of mol fraction $N_2$, the resulting mol fraction N can be written with sufficient accuracy as,

$$N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2a)$$

The error introduced on account of this approximation is easily shown to be negligible (being of the order of 0·6 per cent. when the constituents of the mixture originally contain 50 and 30 per cent. heavy water). It will be smaller still for the low concentration range considered here.

§ 3. Suppose now we start with volume V containing mol fraction $N_0$ of heavy water and reduce it by electrolysis to a volume $V/m$ where $m > 1$ (*vide infra*). The mol fraction $N_1$ of the residue will be given by

$$N_1 = N_0\,(m)^{1-1/\alpha'}$$

Add a volume $V\,(1 - 1/m)$ of mol fraction $N_0$ and thus bring back the volume to its initial volume V. The mol fraction of the resulting homogeneous mixture will be

$$N_{02} = N_0\left(\frac{m-1}{m}\right) + N_1 \cdot \frac{1}{m}$$

Substituting for $N_1$ from above

$$N_{02} = N_0\left\{\frac{m-1}{m} + (m)^{1-1/\alpha'} \cdot \frac{1}{m}\right\}$$

$$= N_0\left\{\frac{m-1}{m} + \left(\frac{1}{m}\right)^{1/\alpha'}\right\}.$$

In the second stage, we proceed as before; starting with volume V of mol fraction $N_{02}$ we reduce it by electrolysis to a volume $V/m$ (where $m$ is the same number as before). Now, add to this a volume $V\left(1 - \frac{1}{m}\right)$ and thus bring back the volume to V and so on. If we go on repeating this process $n$ times the final residue will have a mol fraction $N_n$ given by

$$N_n = N_0\,(m)^{1-1/\alpha'}\left\{\frac{m-1}{m}\left[1 + \left(\frac{1}{m}\right)^{1/\alpha'} + \left(\frac{1}{m}\right)^{2/\alpha'} + .. + \left(\frac{1}{m}\right)^{n-2/\alpha'}\right] + \left(\frac{1}{m}\right)^{n-1/\alpha'}\right\} \quad .. \quad .. \quad (3)$$

§ 4. As a result of this $n$-stage process we have reduced a total volume $V + V\frac{m-1}{m} \cdot n$ to a final volume $\frac{V}{m}$. Instead of doing this in stages, if

one had started with an initial volume $V\left(1 + n \cdot \frac{m-1}{m}\right)$ and reduced it to $\frac{V}{m}$ in a *single* stage, the mol fraction of heavy water in the residue of this process would have been

$$N = N_0 \left[\left(1 + n \cdot \frac{m-1}{m}\right) m\right]^{1-1/\alpha'}$$

$$= N_0 (m)^{1-1/\alpha'} \left[1 + n \cdot \frac{m-1}{m}\right]^{1-1/\alpha'} \quad .. \quad .. \quad (4)$$

Therefore,

$$\frac{N - N_n}{N_0} = (m)^{1-1/\alpha'} \left\{\left[1 + n \cdot \frac{m-1}{m}\right]^{1-1/\alpha'} - \left[\frac{m-1}{m}\left\{1 + \left(\frac{1}{m}\right)^{1/\alpha'} + \left(\frac{1}{m}\right)^{2/\alpha'} + \ldots + \left(\frac{1}{m}\right)^{n-2/\alpha'}\right\} + \left(\frac{1}{m}\right)^{n-1/\alpha'}\right]\right\} .. \quad (5)$$

Put $\delta$ = fraction (by volume) electrolysed at each step, *i.e.*, its relative magnitude, then

$$\frac{N - N_n}{N_0} = F = \left(\frac{1}{1-\delta}\right)^{1-1/\alpha'} \left\{\left[1 + n\delta\right]^{1-1/\alpha'} - \left[\delta\left\{1 + (1-\delta)^{1/\alpha'} + \ldots + (1-\delta)^{n-2/\alpha'}\right\} + (1-\delta)^{n-1/\alpha'}\right]\right\} \ldots \quad .. \quad .. \quad .. \quad (6)$$

For small values of $n$ and $\delta$

$$F = \left(\frac{1}{1-\delta}\right)^{1-1/\alpha'} \left\{1 + \left(1 - \frac{1}{\alpha'}\right) n\delta - \left[\delta(n-1) + 1 - \frac{n-1}{\alpha'}\delta\right]\right\}$$

$$= (1+\delta)^{1-1/\alpha'} \left[1 - \frac{1}{\alpha'}\delta\right].$$

For large values of $n$ and $\delta$, however, no further simplification can be introduced in (6).

§ 5. It will be seen from (6) that F, the relative decrease in the yield of heavy water, which is a measure of the efficiency of separation depends upon $\delta$ the magnitude of the relative step, in such a manner that $F \to 0$ as $\delta \to 0$ showing that if water be added *continuously*, *i.e.*, not stagewise, there will be no loss in efficiency. Anderson, Halford and Bates[4] have made use of such a method, and find that no sensible loss in efficiency results in agreement with the above deduction. This result would have been hard to explain on the basis of the existing explanation,[5] "that the continual addition of

fresh-water tends to reach a relatively low *equilibrium* value for the concentration of heavy water".

The following table gives the values of F for different values of $\delta$ assuming that $\alpha' = 3$ and $n = 10$. In the last but one column are given the percentage defects (introduced on account of the stagewise addition of water) in terms of the final values for the mol fraction of heavy water obtained in the single stage process. In the last column are given the apparant values of $\alpha'$ that will be obtained under these circumstances, experimentally.

TABLE I.

| No. | $\delta$ | F | Percentage defect | Apparent value of $\alpha'$ |
|---|---|---|---|---|
| 1 | ·1 | ·07 | 4 | 2·5 |
| 2 | ·2 | ·23 | 10 | 2·4 |
| 3 | ·3 | ·45 | 14 | 2·3 |
| 4 | ·4 | ·98 | 23 | 2·17 |
| 5 | ·5 | 1·68 | 32 | 2·04 |

It will be noticed that the percentage defect will increase rapidly with $n$ as well as $\delta$; it must be remembered, however, that the original assumption, *viz.*, that the proportion of the heavy water in all the processes considered is *low*, sets a natural limit on the values of $n$ and $\delta$.

The equation (1) given by Urey is quite general and may therefore be applied to cases of fractional distillation, etc., the value of $\alpha'$ being appropriate to the process considered. It is to be anticipated, therefore, that the considerations in § 5 might apply correspondingly to these cases. The generality of equation (6), however, is restricted by the approximation, introduced in (2*a*), of the equality of the molar volumes of the two components.

*Summary.*

A quantitative estimate has been given on the basis of Urey's equation, of the decrease in efficiency in the electrolytic separation of heavy water (assumed to be present in small proportions) due to the continual addition of fresh-water in terms of the variables involved. It is shown that compared

with a single stage process, there will be *no less in efficiency*, if fresh-water be added *continuously*. A relation connecting the decrease in efficiency with the relative magnitude of the step has been derived.

REFERENCES.

1. E. W. Washburn, E. R. and F. A. Smith, "Bureau of Standards", *J. of Research*, 1934, **13**, 599.
2. E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci., America*, 1932, **18**, 496.
3. H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, Jan. 1935.
4. L. C. Anderson, J. O. Halford and J. R. Bates, *J. Chem. Phys.*, 1934, **2**, 342.
5. J. H. Wolfenden, *Ann. Reports of the Chemical Society*, London, 1933.

# CONDITION OF SPARINGLY SOLUBLE SUBSTANCES IN GELS.

## Part I. Silver Chromate in Gelatine.

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Williams and Mackenzie,[1] Bolam and co-workers[2] and Desai and Nabar[3] have shown from conductivity and e.m.f. measurements that prior to the appearance of red colour the yellow mixture of silver nitrate and potassium chromate in gelatine contains silver chromate in supersaturated solution and that the red colour is due to the actual formation of the solid phase, and not to the coagulation of a solid phase which is already present in the form of colloidal particles. Dhar and collaborators[4] have, on the other hand, shown from conductivity and diffusion experiments that the yellow mixture contains particles which are negatively charged through adsorption of chromate ions, while the red substance is a less stable sol containing particles which are positively charged through adsorption of silver ions. Naik, Desai and Desai[5] have observed that whatever changes in the conductivity are to occur take place immediately the solutions of silver nitrate in gelatine and potassium chromate in gelatine are mixed and that there is no gradual decrease of conductivity with changes in the colour of the mixures—observation against the views of Bolam and co-workers. The cataphoretic experiments did not show presence of any charged particles either in the yellow or red mixtures—observation against the view of Dhar and co-workers. They have suggested that immediately the solutions are mixed some insoluble substance is produced, the particles of which are in a very highly dispersed condition—probably in molecular condition—and that changes in the colour of the mixtures are due to growth of these very fine particles into larger ones.

The present work was undertaken to find out causes of differences in the results of various investigators about the condition of silver chromate in gelatine.

*Experimental.*

The gelatine used in these experiments contained 1·177% ash and 18% moisture and its $p_H$ (determined colorimetrically) was 5·45. Samples of gelatine having different $p_H$ were prepared by adding suitable amounts of acetic acid and sodium acetate. The conductivity experiments were carried out exactly in the same manner as done by Naik, Desai and Desai.[5] N/100 solutions of $AgNO_3$ and $K_2CrO_4$ and 3% solution of gelatine were used throughout. The reacting mixtures ($AgNO_3$ in gelatine and $K_2CrO_4$ in gelatine) were allowed to attain the required temperature by placing them in an electrically heated thermostat and then mixed by passing from tube to tube several times in a uniform manner ; the mixture was then transferred to the conductivity cell, which was immediately kept in the thermostat for conductivity measurements. The total volume of the mixture in each experiment was 16 c.c. The time when colour change took place was carefully noted. The percentage of silver chromate in ionic condition was calculated exactly in the same manner as before.[5]

On allowing the gelatine solution to stand for different periods it was observed that its inhibitive power (power to prevent appearance of red coloured precipitate of silver chromate from yellow mixture) is not affected to any appreciable extent even when the mixture of gelatine and reactants is kept standing for 72 hours.

*Results and Discussion.*

*A. Changes in the inhibitive power of gelatine and condition of silver chromate at different temperatures.*—In Fig. 1 are plotted the values of conductivity (observed) of silver chromate alone at different times for 4·5 c.c. of reactants at different temperatures. The curves for other concentrations of the reactants are exactly similar. It was observed that in each case the conductivity did not change further on allowing the mixture to stand even for 24 hours or more. A summary of the results of all these experiments is given in the following table.

TABLE I.

Concentration of gelatine = 3%, $p_H$ of gelatine = 5·45.
Total volume = 16 c.c. [2X c.c. of electrolyte + 4·4 c.c. of 3% gelatine + (16 − 2X − 4·4) c.c. conductivity water].

| c.c. of electrolyte (X) | Temperature °C. | % of $Ag_2CrO_4$ in ionic condition before red colour appears | % of $Ag_2CrO_4$ in ionic condition after appearance of red colour and when conductivity does not change further on standing | Time for appearance of red colour in minutes | Time when conductivity begins to decrease in minutes |
|---|---|---|---|---|---|
| 3·5 | 20 | 91 | 59 | 200 | 215 |
| | 30 | 87 | 69 | 300 | 330 |
| | 35 | 86 | 75 | 430 | 470 |
| | 40 | 84 | 84 | 600 | >720 |
| 4·0 | 20 | 88 | 49 | 29 | 30 |
| | 30 | 87 | 57 | 45 | 47 |
| | 40 | 85 | 65 | 90 | 94 |
| | 50 | 84 | 80 | 305 | 340 |
| | 55 | 83 | 83 | 460 | >650 |
| 4·5 | 20 | 87 | 39 | 5 | 5·5 |
| | 30 | 85 | 44 | 8 | 8·5 |
| | 40 | 84 | 51 | 15 | 16 |
| | 50 | 82 | 61 | 28 | 30 |
| | 60 | 80 | 75 | 120 | 160 |
| | 65 | 78 | 78 | 200 | >600 |
| 5·0 | 20 | 77 | 30 | 2 | 2·5 |
| | 30 | 76 | 35 | 3 | 3·5 |
| | 40 | 75 | 41 | 4 | 4·5 |
| | 50 | 74 | 47 | 5 | 6 |
| | 60 | 73 | 53 | 6 | 7 |
| | 65 | 72 | 55 | 7 | 9 |

The following conclusions can be drawn from the results :—

(1) The inhibitive power (time for appearance of red colour) increases with a rise of temperature.

(2) The difference between the times of appearance of red colour and the decrease of conductivity increases with a rise of temperature, the colour change and conductivity decrease occurring more or less simultaneously at relatively low temperatures.

(3) The temperature at which the conductivity does not decrease in spite of colour change even when the mixture is allowed to stand

for 24 hours or more is higher for mixtures containing larger amounts of reactants than those containing smaller amounts.

(4) For each concentration of the reactant the % of $Ag_2CrO_4$ in ionic condition before the appearance of red colour decreases with a rise of temperature, while that after the appearance of the red colour and when conductivity does not decrease any further on standing increases at the same time.

(5) For each temperature the smaller the amount of reactants, the larger the % of $Ag_2CrO_4$ in ionic condition before and after the appearance of red colour.

(6) If the difference between the amounts of silver chromate in ionic condition before and after the appearance of red colour is taken roughly as a measure of degree of supersaturation, it is seen that the degree of supersaturation decreases with an increase of temperature.

(7) In each case at relatively low temperatures the conductivity first remains constant, then decreases for some time and remains constant afterwards (Fig. 1).

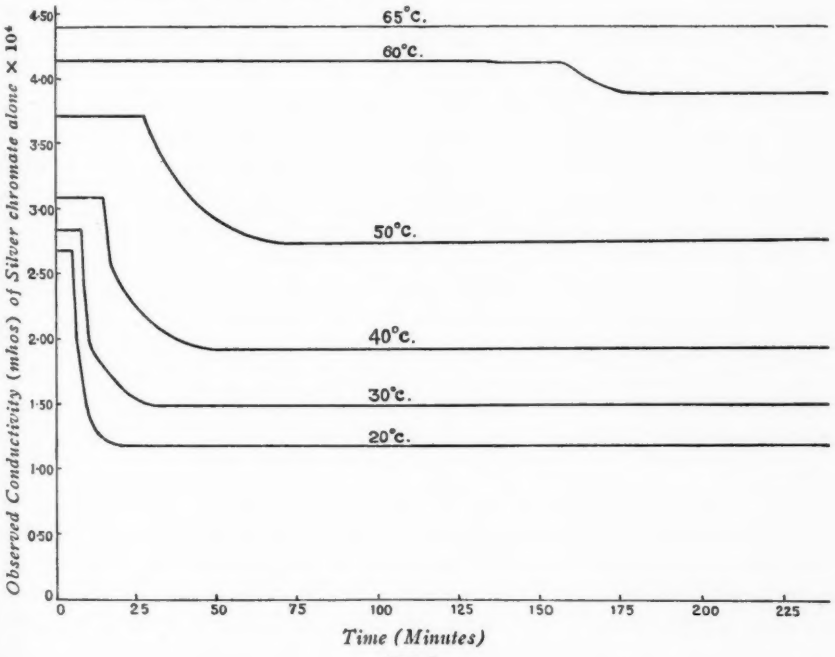


FIG. 1.

It is now proposed to discuss the above changes. (1) One might consider that the increase in the inhibitive power with a rise of temperature might be due to a change in the $p_H$ of gelatine. The measurements of p between temperatures 20° C. and 70° C., however, showed that $p_H$ changes, if any, are very insignificant and therefore cannot be considered to have any appreciable influence on the large inhibitive power of gelatine at relatively high temperatures. An increase in the solubility of $Ag_2CrO_4$ with a rise of temperature cannot also alone explain these changes because although the solubility of $Ag_2CrO_4$ in water at 60° C. is about $2\frac{1}{2}$ times that at 20° C., the inhibitive power has become more than $2\frac{1}{2}$ times within this temperature range as will be seen from Table I. It is likely that the degree of dispersity of gelatine might have increased with a rise of temperature, resulting in an increase of inhibitive power.

(2) At relatively low temperatures the colour change and decrease in conductivity take place more or less simultaneously probably because most of the silver chromate in those cases exists in ionic condition at first and a part of it is thrown out later as red $Ag_2CrO_4$ due to release of supersaturation (*cf.* Bolam and co-workers[2] and Desai and Nabar[3]). In each case at a certain temperature the conductivity does not decrease in spite of appearance of red coloured precipitate because a small portion of the silver chromate probably exists in a very highly dispersed condition—may be even molecularly dispersed—in the yellow mixture and the appearance of red colour is probably due to formation of molecular aggregates, conductivity not decreasing due to absence of supersaturation (*cf.* Naik, Desai and Desai[5]). It may be mentioned that even at relatively low temperatures a slight amount of silver chromate might be existing in highly dispersed condition and these very fine particles probably help release of supersaturation ; the colour change and conductivity decrease occur more or less simultaneously because supersaturation being also relatively great, even very fine particles could help its release. During the intermediate stages the small portion of silver chromate which might be existing in highly dispersed condition in the yellow mixture probably gives rise to molecular aggregates (appearance of red colour), which later act as crystallisation centres for release of supersaturation (decrease of conductivity).

(3) The temperature at which conductivity does not decrease in spite of colour change is higher for mixtures containing large amounts of reactants than those containing smaller amounts probably because the amount of gelatine having remained the same, a higher degree of dispersity of gelatine is necessary in the former case than in the latter in order to increase the inhibitive power. As stated in (1) above, the degree of dispersity of gelatine

probably increases with temperature; a higher temperature is therefore necessary for mixtures having larger amounts of reactants than those containing smaller amounts, other conditions having remained the same.

(4) The % of $Ag_2CrO_4$ in ionic condition in the beginning and before the appearance of red colour decreases with a rise of temperature probably because the degree of dispersity of gelatine having increased [see (1) above], a relatively large amount of $Ag_2CrO_4$ might have either been adsorbed by, or chemically interacted with, gelatine at relatively high temperatures.

The % of $Ag_2CrO_4$ in ionic condition after appearance of red colour increases with a rise of temperature probably because of an increase in the (*a*) solubility of $Ag_2CrO_4$ [see (1) above] and (*b*) inhibitive power of gelatine. As stated in (1) above the increase in inhibitive power is probably due to greater degree of dispersity of gelatine at higher than at lower temperatures; this effect seems to be similar to that of hydrolysis studied by Desai and Nabar,[3] where it was noticed that the final values of the activity of the silver ion increase with an increase in hydrolysis.

(5) This is probably due to the fact that a greater amount of $Ag_2CrO_4$ has either been adsorbed by, or chemically interacted with, gelatine in mixtures containing larger amounts of reactants than those containing smaller amounts.

(6) The degree of supersaturation with an increase of temperature has decreased but the inhibitive power of gelatine increased at the same time. Obviously, as stated by Naik, Desai and Desai,[5] the inhibition experiments cannot always be utilised to give an idea about the degree of supersaturation although they can be in some cases and under certain circumstances. The decrease in the degree of supersaturation with a rise of temperature might probably be due to an increase in the solubility of $Ag_2CrO_4$. The increased adsorption by, or chemical interaction with, gelatine of $Ag_2CrO_4$ at high temperatures might also to a certain extent decrease supersaturation.

(7) The conductivity-time curves are similar to the activity of Ag ion-time curves obtained by Desai and Nabar[3] except for the fact that the point at which the conductivity commences to decrease does not in every case correspond with the first appearance of red colour.

*B. Influence of changes in $p_H$ of gelatine on the condition of silver chromate.*—The nature of the curves obtained on plotting the values of conductivity (observed) of silver chromate alone at different times is similar to that of the conductivity-time curves given in Fig. 1. A summary of the results of these experiments is given in the following table.

TABLE II.

Concentration of gelatine = 3%.

Temperature of experiments = 30° C.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4·4 c.c. of 3% gelatine + (16 − 2X − 4·4) c.c. conductivity water].

| c.c. of electrolyte (X) | pH of gelatine | % of $Ag_2CrO_4$ in ionic condition before red colour appears | % of $Ag_2CrO_4$ in ionic condition after red colour appears and when conductivity does not change further on standing | Time of appearance of red colour in minutes | Time when conductivity begins to decrease in minutes |
|---|---|---|---|---|---|
| 3·5 | 5·45 | 87 | 69 | 300 | 330 |
| | 5·75 | 81 | 58 | 180 | 190 |
| | 6·00 | 77 | 64 | 240 | 267 |
| | 6·25 | 73 | 73 | 300 | >600 |
| 4·0 | 5·25 | 87 | 60 | 120 | 124 |
| | 5·45 | 87 | 57 | 45 | 47 |
| | 5·75 | 68 | 45 | 24 | 25 |
| | 6·00 | 66 | 50 | 32 | 40 |
| | 6·25 | 63 | 55 | 43 | 60 |
| | 6·50 | 60 | 60 | 65 | >240 |
| 4·5 | 5·00 | 84 | 51 | 50 | 54 |
| | 5·25 | 85 | 47 | 22 | 23 |
| | 5·45 | 85 | 44 | 8 | 8·5 |
| | 5·75 | 58 | 32 | 4·5 | 5 |
| | 6·00 | 56 | 37 | 5 | 8 |
| | 6·25 | 53 | 42 | 6 | 15 |
| | 6·50 | 50 | 50 | 10 | >180 |

The following conclusions can be drawn from these results :—

(1) For all the concentrations of reactants the inhibitive power of gelatine is minimum for $p_H$ 5·75, it being greater for higher or lower values of $p_H$.

(2) The difference between the times of appearance of red colour and the decrease of conductivity increases with $p_H$ for samples of gelatine having $p_H$ greater than 5·75; for gelatine samples of $p_H$ smaller than 5·75 this difference increases with decrease of $p_H$ only in those cases where the concentration of the reactants is not too large and the inhibitive power is proportionately great.

(3) For samples of gelatine having $p_H$ greater than 5·75 the greater the concentration of the reactants the higher is generally the $p_H$ at which the colour change appears but the conductivity does not decrease at all.

(4) For each concentration of the reactants the % of $Ag_2CrO_4$ in ionic condition before the appearance of red colour generally decreases regularly with an increase of $p_H$; the % of $Ag_2CrO_4$ in ionic condition after the appearance of red colour and when conductivity does not decrease any further on standing is lowest for $p_H$ value 5·75 for 3·5 and 4·5 c.c. of reactants, and for $p_H$ value 5·45 for 4·0 c.c. of reactants, it being greater for higher or lower values of $p_H$.

(5) For each value of $p_H$ the smaller the amount of the reactants, the larger the % of $Ag_2CrO_4$ in ionic condition before and after the appearance of red colour.

(6) If the difference between the amounts of silver chromate in ionic condition before and after the appearance of red colour is taken roughly as a measure of degree of supersaturation, it is seen that the supersaturation is highest for $p_H$ value 5·75. for 3·5 and 4·5 c.c. of reactants, and for $p_H$ value 5·45 for 4·0 c.c. of reactants, it being smaller for higher or lower values of $p_H$.

The causes of these changes may now be discussed.

(1) The results support the observation of Desai and Naik[6] that the inhibitive power of gelatine with reference to $p_H$ 5·75 is minimum, it being higher for samples of gelatine having greater or smaller $p_H$. The causes of minimum inhibitive power for $p_H$ 5·75 are not clear. It may be that the degree of dispersity of gelatine at this $p_H$ might be lowest.

(2) The colour change and decrease in conductivity occur more or less simultaneously in all cases for $p_H$ 5·75. It will appear from conclusion (6) that the degree of supersaturation is also highest in samples of gelatine having $p_H$ near about 5·75. It is likely that a small amount of $Ag_2CrO_4$ which might be present in molecularly dispersed condition from the beginning helps in releasing supersaturation. For higher or lower values of $p_H$ the degree of supersaturation decreases; at sufficiently low or high values of $p_H$ characteristic of each concentration of the reactants, there will not be any supersaturation and therefore the colour changes which will occur in these cases will be due to formation of molecular aggregates from $Ag_2CrO_4$ which probably exists in molecularly dispersed condition from the beginning. It is clear from these results that for each concentration of the reactants the colour change and decrease in conductivity will occur more or less simultaneously for $p_H$ 5·75; *i.e.*, the $p_H$ is gradually lowered below or raised

above 5·75, the difference between the times of colour change and decrease of conductivity will continuously increase, and ultimately at certain values of $p_H$ higher and lower than 5·75—characteristic of each concentration of the reactants, the conductivity will not decrease at all in spite of colour change.

(3) This is probably due to the fact that for relatively high concentrations of the reactants, the amount of gelatine having remained the same, the $p_H$ will have to be increased relatively to a large extent in order to increase the inhibitive power. From the trend of the present results it appears that for samples of gelatine having $p_H$ smaller than 5·75, the higher the concentration of the reactants the lower will generally be the $p_H$ at which the colour change will occur but the conductivity will not decrease at all.

(4) The % of $Ag_2CrO_4$ in ionic condition before the appearance of red colour decreases with increase of $p_H$ probably because a relatively large amount of $Ag_2CrO_4$ might have either been adsorbed by, or chemically interacted with, gelatine at relatively high values of $p_H$.

The % of $Ag_2CrO_4$ in ionic condition after the appearance of red colour is lower for $p_H$ 5·75 probably because the inhibitive power being minimum, a relatively large amount of $Ag_2CrO_4$ is thrown out in condition other than ionic.

(5) The causes of this might be similar to those given under (5) in Section (A).

(6) The fact that gelatine samples of $p_H$ near about 5·75 show higher supersaturation than those with higher or lower $p_H$ in spite of minimum inhibitive power support the view stated before, namely, that the experiments on inhibitive power should not be utilised to get idea about degree of supersaturation.

On page 876 of their paper, Bolam and Donaldson[2] have calculated the degree of supersaturation according to the theory of von Weimarn and found that the degree of supersaturation increases slightly as the $p_H$ decreases from 5·7 to 5·0, and then falls off more rapidly as the $p_H$ is further decreased. They conclude that the degree of supersaturation and therefore the inhibitive action of gelatine, probably has an optimum value at $p_H$ 5·0. The present results do not support the conclusion of Bolam and Donaldson.

*C. Determination of temperatures at which colour change occurs but conductivity does not decrease at all in mixtures of silver chromate in gelatine of different* $p_H$.—The results of these experiments are given in the following table.

TABLE III.

Concentration of gelatine = 3%.

Total volume = 16 c.c. [2X c.c. of electrolyte + 4·4 c. c. of 3% gelatine + (16 − 2X − 4·4) c.c. conductivity water].

| c.c. of electrolyte (X) | $p_H$ of gelatine | Temperature at which red colour appears but conductivity does not change |
|---|---|---|
| 3·5 | 5·45 | 40° C. |
| | 5·75 | 50 |
| | 6·00 | 40 |
| | 6·25 | 30 |
| 4·0 | 5·25 | 50 |
| | 5·45 | 55 |
| | 5·75 | 60 |
| | 6·00 | 50 |
| | 6·25 | 40 |
| 4·5 | 5·00 | 55 |
| | 5·25 | 60 |
| | 5·45 | 65* |
| | 5·75 | 65 |
| | 6·00 | 55 |
| | 6·25 | 45 |

* The temperature, at which colour change occurs but conductivity does not decrease might be about 62° to 63° C. in this case.

It will appear from the table that for each concentration of the reactants the temperature at which no change in conductivity will occur in spite of a change in colour is highest for gelatine of $p_H$ 5·75, it being lower for higher or lower values of $p_H$. It has been stated in Section B that the inhibitive power of gelatine is minimum for $p_H$ 5·75. In Section A it is suggested that the degree of dispersity of gelatine might be increasing with a rise of temperature. It thus appears possible that the degree of dispersity of gelatine might be smallest for $p_H$ 5·75—hence minimum inhibitive power—because the temperature at which colour change occurs but conductivity does not decrease is highest for that value of $p_H$. There is, however, no direct evidence to support this statement.

In each case for temperatures lower than those given in Table III, the conductivity will decrease either simultaneously with a change of colour or sometime after it.

*D. Influence of changes in concentration of gelatine on the conductivity of silver chromate.*—The results of these experiments are given in Table IV.

TABLE IV.

Temperature of experiments = 30° C.

$p_H$ of gelatine = 5·45.

Total volume = 16 c.c. [2X c.c. of electrolyte + 2Z c.c. of 3% gelatine + (16 − 2X − 2Z) c.c. of conductivity water].

| c.c. of electrolyte (X) | c.c. of 3% gelatine (Z) | % of $Ag_2CrO_4$ in ionic condition before red colour appears | % of $Ag_2CrO_4$ in ionic condition after red colour appears and when conductivity does not change further on standing | Time for appearance of red colour in minutes | Time when conductivity begins to decrease in minutes |
|---|---|---|---|---|---|
| 3·5 | 1·0 | 95 | 43 | 5 | 6 |
| | 1·5 | 92 | 51 | 52 | 54 |
| | 2·0 | 89 | 60 | 225 | 250 |
| | 2·2 | 87 | 69 | 300 | 330 |

It will appear that the time for the appearance of red colour increases with an increase in the amount of gelatine and that although the colour change and decrease in conductivity occur more or less simultaneously when the amounts of gelatine are relatively small, the conductivity decrease occurs later and later than colour change as the amount of gelatine increases. These changes become intelligible if we examine the values given in columns 3 and 4 of the table ; the degree of supersaturation, as judged roughly from the difference in the values of % of silver chromate in ionic condition before and after the appearance of red colour, has decreased with an increase in the amount of $p_H$.

From the trend of the values given in columns 3 and 4 it will be clear that for a certain amount of gelatine (more than that contained in 4·4 c.c. of 3% gelatine solution), the % of silver chromate before and after the appearance of red colour will be the same, *i.e.*, the conductivity will not decrease in spite of appearnce of red colour. This amount of gelatine will be different for different concentrations of the reactants.

The percentage of silver chromate in ionic condition before the appearance of red colour decreases with an increase in the amount of gelatine. This

is due to the fact that as the amount of gelatine increases the amount of silver chromate removed by it either as a result of adsorption or chemical interaction also increases.

The continuous increase in the percentage of silver chromate in ionic condition after the appearance of red colour with an increase in the amount of gelatine is due to the fact that a relatively large amount of silver chromate is thrown out when the amount of gelatine is relatively small.

*Summary.*

Changes in the conductivity and colour of silver chromate in gelatine solution have been studied. It is observed that by suitable adjustment of the (i) temperature of the experiments, (ii) $p_H$ of gelatine, (iii) concentration of the reactants ($AgNO_3$ and $K_2CrO_4$) and (iv) amount of gelatine, the conductivity may (*a*) not decrease at all till the colour remains yellow, (*b*) decrease sometime after the colour change or (*c*) not change at all in spite of the colour change.

In the end we would like to mention that our preliminary experiments on the precipitation of lead iodide in agar have shown that the (*a*) temperature at which the experiments are carried out, (*b*) $p_H$ of agar, (*c*) amount of agar and (*d*) concentration of the reactants [$Pb(NO_3)_2$ and KI) have a very marked influence upon the times when the colour change and decrease in conductivity take place[7] as in the case of precipitation of silver chromate in gelatine.

REFERENCES.

1 Williams and Mackenzie, *J. C. S.*, 1920, **117**, 844.

2 Bolam and Mackenzie, *Trans. Faraday Soc.*, 1926, **22**, 162; *ibid.*, 1928, **24**, 50; Bolam and Donaldson, *ibid.*, 1933, **29**, 864.

3 Desai and Nabar, *Trans. Faraday Soc.*, 1932, **28**, 449.

4 Dhar and co-workers, *J. Phys. Chem.*, 1924, **28**, 41; *Kolloid. Z.*, 1924, **34**, 270; *Trans. Faraday Soc.*, 1927, **23**, 23; *J. Indian Chem. Soc.*, 1928, **5**, 175.

5 B. M. Naik, H. N. Desai and B. N. Desai, *J. Indian Chem. Soc.*, 1934, **11**, 45.

6 Desai and Naik, *J. Univ. Bombay*, 1933, **2** (2), 90.

7 See in this connection Bolam, *Trans. Faraday Soc.*, 1928, **24**, 463; *ibid.*, 1930, **26**, 133; and Chatterjee and Dhar, *J. Indian Chem. Soc.*, 1930, **7**, 177.

# IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

## Part III. Colloidal Prussian Blue.

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In papers published by Desai and collaborators[1] it has been shown that changes which are produced in the charge on colloidal particles during dialysis are not so simple as is usually supposed and that the results of viscosity and stability cannot always be utilised for getting an idea about the charge on colloid particles. The results of simultaneous measurements of cataphoretic speed, stability and viscosity of colloidal solutions of ferric and thorium hydroxide have been given in Parts I (Desai and Borkar[1]) and II (B. N. Desai and A. K. Desai[1]) respectively. It will be seen from the results that the behaviour of both the sols as regards dialysis, dilution and critical potential is similar; the viscosity changes on dialysis and in presence of electrolytes have, however, been found to be different. In the present paper similar simultaneous measurements taken with colloidal prussian blue are presented.

### *Experimental.*

Prussian blue was precipitated by adding slowly and without stirring a 2% solution of potassium ferrocyanide to a 2% solution of ferric chloride.[2] The precipitate was allowed to stand for about 15 minutes, filtered and peptised by shaking vigorously with a 2% oxalic acid solution in one case and a 5% oxalic acid solution in the other. The sol so obtained was filtered four times through a double-fold of filter in order to attain as far as possible uniformity of particle size and better constancy of conductivity.[3]

The sol was dialysed in parchment paper bags which were previously kept soaked in distilled water for 3 to 4 days. The outer water was changed once a day. No prussian blue passed out during dialysis; oxalic acid and traces of ferric chloride were however detected in the dialysate. Dialysis was carried out in dark room in order to avoid effect of light on the sol. The amount of prussian blue in the sol did not change to any appreciable extent during dialysis.

The cataphoretic speed was measured by Mukherjee's improved U-tube method. The dialysate made equi-conducting by addition of potassium chloride in the initial stages of dialysis and by addition of oxalic acid in the later stages was found to be quite satisfactory as an upper liquid. The difference between the direct and reverse movements of the boundary was never more than 3 to 4%. In all the tables of results, the cataphoretic speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre $\times 10^5$. The concentration of the electrolytes is expressed in millimoles per litre.

Viscosity was measured by using an Ostwald viscometer. The results of viscosity have been expressed in terms of the viscosity of distilled water at the temperature of the experiment as unity.

The stability was determined by finding out the amount of the electrolyte necessary to give instantaneous coagulation. The flocculation values are expressed in millimoles of the electrolyte in total volume, *i.e.*, 30 c.c.'s in this case.

All the measurements of cataphoretic speed and viscosity were made at a temperature of 30° C.

*Results and Discussion.*

*A. Effect of ageing.*—Sols dialysed for 6 and 25 days were removed and stocked in resistance glass flasks covered with black paper and the cataphoretic speed (cat. speed) was determined at different periods. The results are given in the following table :—

TABLE I.

| Sol dialysed for 6 days | | Sol dialysed for 25 days | |
|---|---|---|---|
| Age in days | Cat. speed | Age in days | Cat. speed |
| 0 | 39·20 | 0 | 38·60 |
| 30 | 37·00 | 20 | 38·30 |
| 40 | 36·90 | 38 | 31·55 |
| 143 | 36·90 | 104 | 27·90 |
| 216 | 36·60 | 173 | 27·40 |
| 262 | 36·00 | 218 | 27·20 |

It will appear that in the case of the sol dialysed for 6 days, the cat. speed first decreases and then remains constant for a certain period after

which it again decreases, while for the sol dialysed for 25 days, the cat. speed first decreases very slowly, then rapidly and afterwards again slowly when kept for longer periods. The decrease in the cat. speed on ageing might possibly be due to preferential adsorption of the coagulating ions.

In order to minimise the effect of ageing, all the experiments were carried out in as short a time as possible.

*B. Changes in cataphoretic speed, stability and viscosity with the progress of dialysis.*—The results of these experiments are given in Tables II and III.

TABLE II.

*Sol peptised with 5% oxalic acid solution.*

| Period of dialysis in days | Cat. speed | Relative viscosity | Flocculation values with KCl |
|---|---|---|---|
| 3 | 38·10 | 1·027 | 7·06 |
| 6 | 41·60 | 1·000 | 5·80 |
| 10 | 42·05 | 0·996 | 4·20 |
| 12 | 42·90 | 1·005 | 2·74 |
| 15 | 50·30 | 1·008 | 1·20 |
| 19 | 21·50 | 1·009 | 0·50 |
| 23 | 13·10 | 1·014 | 0·10 |

TABLE III.

*Sol peptised with 2% oxalic acid solution.*

| Period of dialysis in days | Cat. speed | Relative viscosity | Flocculation values with KCl |
|---|---|---|---|
| 4 | 39·00 | 1·014 | 4·84 |
| 9 | 41·10 | 1·009 | 4·20 |
| 14 | 44·10 | 1·004 | 2·64 |
| 18 | 43·60 | 1·005 | 1·28 |
| 27 | 38·00 | 1·012 | .. |
| 30 | 27·00 | 1·014 | .. |
| 34 | 19·50 | .. | .. |

It will appear from Tables II and III that with the progress of dialysis the cat. speed first increases and reaches a maximum after which it gradually decreases, while the relative viscosity first decreases and reaches a minimum after which it gradually increases. The stability as determined by flocculation values with KCl continuously decreases with the progress of dialysis.

Desai and co-workers[1] have explained a first increase and then a decrease in the cat. speed with dialysis by assuming that the process of dialysis (during which the amount of peptising agent in the sol continuously decreases) can be considered roughly as a reverse of the process of adding small increasing amounts of the peptising agent to the colloid so far as the influence of the electrolyte on the cat. speed is concerned. If this analogy is correct one would expect that on adding small increasing amounts of oxalic acid, which is the peptising agent in the present case, to the prussian blue sol, the cat. speed should first increase and then decrease. That this is actually the case will be clearly seen from the results given in Table IV.

TABLE IV.

*Cat. speed of colloidal prussian blue (peptised with 2% oxalic acid solution and dialysed for 25 days) in the presence of varying amounts of oxalic acid.*

| Amount of oxalic acid | Cat. speed |
|---|---|
| 0·000 | 26·95 |
| 0·013 | 35·00 |
| 0·037 | 37·50 |
| 0·125 | 39·40 |
| 0·250 | 40·80 |
| 1·250 | 35·70 |
| 3·750 | 31·90 |
| 12·500 | 30·70 |

It will also appear that the cat. speed and the stability do not apparently go hand in hand till the maximum value of charge is reached during dialysis as in the case of ferric and thorium hydroxide sols investigated by Desai and co-workers.[1] In the present case, the decrease in the flocculation values with the progress of dialysis in spite of an increase in charge might be due to an increase in the preferential adsorption of the stabilising (oxalate) ions in the presence of KCl (electrolyte added for flocculation value determinations) as well as a change in the size of the colloid particles during dialysis.

According to v. Smoluchowski,[4] the greater the electric charge on the colloidal particles the greater will be the viscosity of the sol, while according to Dhar and co-workers,[5] other things being identical, a decrease in electric charge on colloid particles causes an increase in hydration and necessarily in the viscosity of the sol. From the results given in Table III it will appear that the viscosity and cat. speed changes with the progress of dialysis completely support Dhar's view, but in the case of the sol peptised with 5% oxalic acid the maximum in the cat. speed and minimum in viscosity have not occurred at the same stage of dialysis—a fact against Dhar's view. The results do not support v. Smoluchowski's view.

On comparing the results given in Tables II and III it will appear that a higher value of cat. speed is obtained for the sol peptised with 5% oxalic acid solution than for the one peptised with 2% oxalic acid solution. There is an advantage in peptising prussian blue with concentrated solution of oxalic acid in that sols so obtained have finer particles and are more stable than those obtained by using dilute solutions of oxalic acid. The sols peptised with concentrated solutions of oxalic acid are, however, not suitable for charge measurements as the boundary becomes diffused due to the disturbances caused by vigorous electrolysis once the current is passed through the sol. In the experiments to be described further only prussian blue sols prepared by using 2% oxalic acid solution have therefore been used.

*C. Changes in the cataphoretic speed and stability of colloidal prussian blue dialysed and diluted to different extents.*—Sols of different concentrations were prepared by adding requisite amounts of conductivity water to the original dialysed sol. The original sol has dilution 1; dilutions of other sols have been obtained from the value of the ratio $\frac{\text{total volume of the diluted sol}}{\text{actual volume of the original sol}}$. The results of these experiments are given in the following table.

TABLE V.

*Figures in columns 'a' and 'b' give values of cat. speed and flocculation (with KCl) respectively.*

| Period of dialysis in days | Dilution | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | 1·33 | | 2 | | 4 | | 5·33 | 8 | |
| | *a* | *b* | *a* | *b* | *a* | *b* | *a* | *b* | *a* | *a* | *b* |
| 3 | 38·70 | 5·20 | 40·30 | 4·70 | 42·50 | 4·16 | 39·00 | 3·36 | 35·75 | 30·10 | 3·16 |
| 8 | 40·60 | 4·32 | 41·10 | 4·04 | 41·10 | 3·50 | 37·70 | 2·58 | 35·00 | 30·10 | 2·20 |
| 13 | 43·20 | 3·24 | 42·20 | 2·84 | 40·50 | 2·20 | 36·10 | 1.12 | 33·80 | 28·60 | 0·36 |
| 17 | 42·50 | 1·70 | 40·90 | 1·28 | 38·70 | 0·66 | 35·00 | 0·14 | 32·50 | 27·00 | .. |
| 21 | 41·05 | .. | 40·00 | .. | 37·60 | .. | 33·60 | .. | 31·30 | 25·90 | .. |
| 26 | 37·10 | .. | 35·40 | .. | 32·30 | .. | 24·20 | .. | 22·30 | 21·50 | .. |
| 30 | 27·50 | .. | 25·80 | .. | 23·05 | .. | 21·00 | .. | 20·60 | .. | .. |

The following conclusions can be drawn from the results given in the table :—

(1) With the progress of dialysis the cat. speed (vertical columns '*a*') first increases and then decreases for sols having dilutions 1 and 1·33, while it continuously decreases for sols having dilutions 2, 4, 5·33 and 8.

(2) On diluting the sol, the cat. speed (values given in columns '*a*'—horizontal rows) first increases and then decreases for sols dialysed for 3 and 8 days, while it continuously decreases for sols dialysed for 13, 17, 21, 26 and 30 days.

(3) The stability of the sol as determined by flocculation values (given in columns '*b*') continuously decreases with the progress of dialysis (vertical columns) and dilution (horizontal rows).

These results are thus exactly similar to those obtained with colloidal ferric and thorium hydroxide.[1] The changes in cat. speed on dilution have been explained by Desai and co-workers[1] by assuming similarity between processes of dilution and dialysis so far as the changes in the amount of the peptising electrolyte are concerned (the amount of the electrolyte in the sol decreases both during dialysis and dilution). According to this view samples of the sol which contain initially an amount of the peptising electrolyte more than that corresponding to the maximum in the cat. speed—concentration curve with that particular electrolyte (in this case the curve

obtained by plotting results given in Table IV) will show first an increase and then a decrease in cat. speed on further dialysing or diluting the sol; samples of sol which contain initially an amount of the peptising electrolyte equal to or less than that corresponding to the maximum in the cat. speed concentration curve of the colloid with that particular electrolyte will show a continuous decrease in cat. speed on further dialysing or diluting the sol. Further according to their view the maximum value of the cat. speed should occur at smaller and smaller dilution with the progress of dialysis and that the maximum value of cat. speed on dialysis should not differ appreciably from the maximum value of cat. speed on dilution. The present results completely support their view-point because (i) the maximum value of cat. speed on dialysis having occurred either on the 13th day or betwen the 8th and 13th day, the cat. speed on dilution has first increased and then decreased in the case of sols dialysed for 3 and 8 days and continuously decreased for sols dialysed for 13 days or longer, (ii) there is no appreciable difference between the maximum value on dialysis, *i.e.*, 43·20 and dilution, *i.e.*, 42·50, and (iii) the maximum value of the cat. speed has occurred at dilution 2 for sol dialysed for 2 days, and between 1·33 and 2 for that dialysed for 8 days.

It is also clear from the results that changes in stability on dilution and dialysis do not always give an idea about changes in cat. speed of the colloidal particles.

It may be mentioned here that for prussian blue dialysed for 3, 8 and 13 days, on diluting the sol the viscosity is found to decrease first rapidly and then slowly and afterwards shows a tendency to become constant. In the case of sols dialysed for periods longer than 13 days, on diluting the sol the viscosity first decreases and then increases. From changes in the cat. speed on dilution of sols dialysed to different extents (Table V) it will be clear that neither the view of Dhar[5] nor of v. Smoluchowski,[4] can individually explain the changes in cat. speed and viscosity observed in these experiments. As stated by Desai and co-workers,[1] one should also consider changes in hydration, the amount of electrolyte and the shape and size of particles to explain these results.

*D. Measurements of cataphoretic speed from the point of view of critical potential.*—A summary of results obtained in these experiments is given in Table VI.

TABLE VI.

| Electrolyte | Initial cat. speed | Initial increase of cat. speed | Cat. speed at which coagulation begins | Concentration of electrolyte at which coagulation begins |
|---|---|---|---|---|
| HCl | 38·70 | 3·60 | 27·50 | 0·125 |
| KCl | 37·30 | 7·30 | 26·20 | 2·500 |
| $MgCl_2$* | 37·05 | nil | 27·85 | 0·075 |
| | 36·35 | nil | 26·75 | 0·750 |
| $MgSO_4$* | 27·90 | nil | 22·20 | 0·125 |
| | 36·90 | nil | 24·50 | 1·250 |

* Results taken with two different samples of sol.

It will appear from the results that in the case of the electrolytes with univalent coagulating ions the cataphoretic speed first increases and then decreases when small increasing amounts of electrolyte are added to the sol, while with electrolytes with bivalent coagulating ions, the initial increase is not noticed at all. The initial increase in cat. speed is due to preferential adsorption of the similarly charged ions as stated before. The preferential adsorption of the similarly charged ions is not observed with $MgCl_2$ and $MgSO_4$ because of the bivalency of the coagulating ions.[1] Further as H-ions act as better coagulating agent than K-ions the initial increase in the cat. speed is smaller in the former case than in the latter.

The value of the cat. speed at which coagulation begins in different cases lies between 22·20 and 27·85, the maximum difference in the initial cat. speed being 10·80. According to Powis[6] coagulation begins only when the electrokinetic potential or the electric charge is lowered to a certain absolute value characteristic of each colloid. Mukherjee and co-workers[7] have, however, concluded that there is no critical potential characteristic of coagulation of a colloid by an electrolyte as suggested by Powis. Desai and co-workers[1] have observed that in the case of the colloidal ferric and thorium hydroxide coagulation begins at about the same value of the cat. speed for different electrolytes although the concentration of the electrolyte corresponding to that cat. speed is quite different in different cases. The present results also support the idea of critical potential at least for the electrolytes tried in this investigation because coagulation has begun at about the same value of cat. speed in different cases ; slight variations in the critical values might be

due to the differences in the nature of the stabilising ions as suggested by Desai and co-workers.[1]

*E. Influence of sunlight on cataphoretic speed of colloidal prussian blue dialysed to different extents.*—For these experiments equal volumes of sol were removed in resistance glass beakers (of same capacity) which were kept covered with glass plates and exposed to sunlight for different periods. Any loss due to evaporation was made good by addition of conductivity water. The results of these experiments are given in Table VII.

TABLE VII.

| Sol dialysed for 10 days | | Sol dialysed for 21 days | |
|---|---|---|---|
| Exposure in hours | Cat. speed | Exposure in hours | Cat. speed |
| 0 | 44·30 | 0 | 42·70 |
| 1 | 43·90 | 1 | 37·80 |
| 3 | 37·90 | 2 | 36·20 |
| | | 5 | 34·10 |
| | | 10 | 33·60 |
| | | 29 | 27·60 |

It will appear from the results that the cat. speed decreases on exposure to sunlight. According to Miss S. Roy and Dhar[8] the prussian blue sol becomes more stable (stability as determined by flocculation values) on exposure to light. They have further stated that the greater stability is due to agglomeration as inferred from the absorption-spectra of sol exposed to sunlight. It is not clear how stability can increase as a result of agglomeration because ordinarily one would expect that the greater the size of particles the smaller the stability of the sol as a smaller amount of electrolyte would be required to reach a given degree of turbidity when the particles are big than when they are relatively small. The fact that agglomeration takes place on exposure will also be supported by the following observations.

TABLE VIII.

| Period of dialysis in days | Time after which sol coagulates on exposure |
|---|---|
| 0 | 1 to 1·5 mins. |
| 1 | 2·5 to 3 ,, |
| 7 | 17 ,, |
| 10 | 3 to 4 hours |
| 21 | > 29 ,, |

It will appear that in the first four cases exposure has given rise to agglomeration, *i.e.*, coagulation. Agglomeration has however resulted in a decrease of stability—a fact not agreeing with observations of Miss S. Roy and Dhar.[8] In the case of the sol dialysed for 21 days no sign of coagulation appears even on exposing it for 29 hours.

According to Laderer and Hartleb,[9] Berlin blue hydrosols are decolourised when exposed to visible light. It may be stated that in our case no decolourisation of the sol was noticed upto an exposure of 29 hours to sunlight, in the case of sol dialysed for 21 days. They have, however, stated that electrolytes decrease the time of flocculation by irradiation. This observation is supported by the results given in Table VIII because the sol dialysed for 21 days and containing very little of oxalic acid does not coagulate even on exposure of 29 hours, while sols dialysed for shorter periods and containing relatively large amounts of oxalic acid coagulate on exposure to sunlight even for very short periods.

The changes in cat. speed on exposure are probably due to action of sunlight on oxalic acid which gives rise to a change in the nature of the intermicellary liquid.

It may be mentioned that viscosity of the sol is found to decrease on exposure to sunlight—a fact which would seem to support v. Smoluchowski's view.

*Summary.*

The cat. speed of colloidal prussian blue (prepared by peptisation with oxalic acid) with the progress of dialysis first increases and then decreases, while the stability as determined by flocculation values with KCl

continuously decreases. The cat. speed on dilution first increases and then decreases in some cases while it continuously decreases in others; the stability on dilution is found to decrease continuously in all the cases. These results of dialysis and dilution are exactly similar to those obtained with colloidal ferric and thorium hydroxide investigated by Desai and co-workers.

The changes in the cat. speed and viscosity under different conditions show that neither the view of Dhar nor of v. Smoluchowski can individually explain the results.

The idea of critical potential is supported.

The cat. speed of the sol decreases on ageing and exposure to sunlight, sols dialysed for short periods even coagulating when exposed to sunlight for a couple of minutes.

REFERENCES.

1. Desai, Nabar and Barve, *J. Indian Chem. Soc.*, 1932, **9**, 463; Desai, *Special Number, J. Indian Chem. Soc.*, 1933, p. 37; Desai and Borkar, *Trans. Faraday Soc.*, 1933, **29**, 1269; Desai, *J. Univ. Bombay*, 1933, **2**, part II, p. 265; B. N. Desai and A. K. Desai, *Trans. Faraday Soc.*, 1934, **30**, 265.
2. Moller, *J. Prakt. Chem.*, 1922, **104**, 241.
3. Annetts, *J. Phys. Chem.*, 1932, **36**, 2936.
4. v. Smoluchowski, *Koll. Z.*, 1916, **18**, 194; also see Kruyt, *Koll. Chem. Beih.*, 1929, **28**, 1; *ibid.*, 1929, **29**, 413.
5. Dhar and co-workers, *J. Phys. Chem.*, 1926, **30**, 1646; *J. Indian Chem. Soc.*, 1929, **6**, 141; *ibid.*, 1932, **9**, 315, 441, 455 and other papers.
6. Powis, *Z. Physik. Chem.*, 1915, **89**, 186.
7. Mukherjee and co-workers, *J. Indian Chem. Soc.*, 1927, **4**, 493; *ibid.*, 1928, **5**, 697 and other papers.
8. Miss Shila Roy and Dhar, *J. Phys. Chem.*, 1930, **34**, 122.
9. Laderer and Hartleb, *Koll. Z.*, 1933, **62**, 42.

# UPLIFT PRESSURES UNDER WEIRS WITH THREE SHEET PILES.

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## *Introduction.*

In a series of papers published in these *Proceedings*[1] and in the *Memoirs of the Punjab Irrigation Research Institute*,[2] the results of extensive investigations on uplift pressures under simple floors, under weirs with one sheet pile[3] and under weirs with two sheet piles[4] have been reported. In the present paper, the investigation has been extended to the case of weirs with three sheet piles. This case is of considerable practical importance, as many of the weirs constructed in India and abroad have three or even four sheet piles.

## *Experimental.*

The technique of the method employed is essentially the same as that described in the first paper of the series.[1] In all the cases investigated, the impervious floor BF in the model (Fig. 1) was 12″ long. Each of the two sheet piles $l_1$ and $l_3$ at the heel and the toe, was 2″ long and their position and length were not altered throughout the investigation. The varying factor was the intermediate sheet pile $l_2$, the length and position of which was altered.

In the first set of observations, the sheet pile $l_2$ was fixed half way between the heel and the toe sheet piles and seven cases were investigated, the length of $l_2$ in each case being 0·5″, 1·0″, 1·5″, 2·0″, 3·0″, 4·0″ and 5·0″. In the second set of observations, the sheet pile $l_2$ was shifted by 1·5″ towards the heel sheet pile $l_1$, and the effect of varying its length on the uplift pressures was investigated as before. Two similar sets of observations were taken by shifting the intermediate sheet pile $l_2$ towards the heel sheet pile $l_1$ in two equal steps of 1·5″. The four positions of the sheet pile $l_2$ are shown

by the lines CD, $C_1D_1$, $C_2D_2$ and $C_3D_3$ in Fig. 1. Thus a total number of twenty-eight cases was investigated. Equi-potential lines were plotted for decrements of 5% of pressure. One set of pressure contours is shown in Fig. 2,

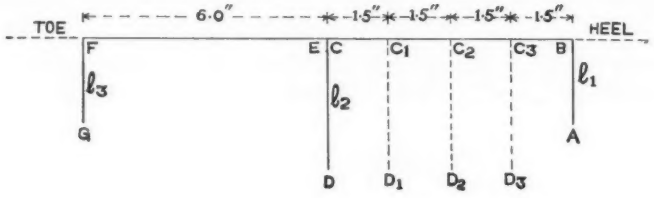


FIG. 1.

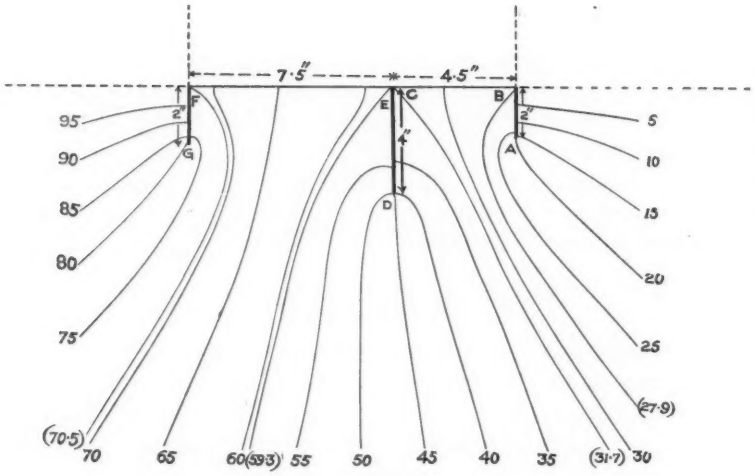


FIG. 2.

as an illustration. For the purpose of design it is sufficient to know the hydraulic gradient under the floor and the pressures at certain points A, B, C, D, E, F and G (Fig. 1) which are reference points in connection with design. These pressures are shown below in the results.

*Results.*

The pressures at the points A, B, C, D, E, F and G are given in tables I–IV and the variation of pressure from point to point under the floor in Figs. 3–6.

TABLE I.

$L = 12 \cdot 0''$, $l_1 = l_3 = 2 \cdot 0''$, $d_1 = d_2 = 6 \cdot 0''$.

Pressures at

| $l_2$ | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 0·5″ | 76·7 | 66·3 | 52·5 | 50·0 | 47·7 | 33·5 | 22·7 |
| 1·0 | 76·8 | 66·7 | 53·7 | 50·0 | 45·9 | 32·7 | 22·7 |
| 1·5 | 76·9 | 67·2 | 55·9 | 50·0 | 44·2 | 32·5 | 22·4 |
| 2·0 | 77·0 | 67·4 | 57·5 | 50·0 | 42·3 | 32·1 | 22·1 |
| 3·0 | 77·5 | 69·1 | 60·7 | 50·0 | 39·1 | 30·7 | 21·4 |
| 4·0 | 78·7 | 70·9 | 63·4 | 50·0 | 36·1 | 28·6 | 20·8 |
| 5·0 | 80·0 | 72·5 | 66·1 | 50·0 | 33·6 | 27·0 | 19·6 |

TABLE II.

$L = 12 \cdot 0''$, $l_1 = l_3 = 2 \cdot 0''$, $d_1 = 4 \cdot 5''$, $d_2 = 7 \cdot 5''$.

Pressures at

| $l_2$ | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 0·5″ | 76·8 | 66·8 | 57·2 | 55·0 | 53·0 | 33·2 | 22·8 |
| 1·0 | 76·8 | 66·9 | 58·9 | 55·1 | 51·2 | 33·2 | 22·8 |
| 1·5 | 76·9 | 67·9 | 60·5 | 55·1 | 49·7 | 32·9 | 22·7 |
| 2·0 | 77·1 | 68·3 | 62·3 | 55·3 | 47·7 | 32·5 | 22·8 |
| 3·0 | 77·7 | 70·5 | 64·9 | 54·5 | 44·6 | 31·3 | 22·1 |
| 4·0 | 78·6 | 72·1 | 68·3 | 54·5 | 40·7 | 29·5 | 20·8 |
| 5·0 | 81·0 | 74·4 | 71·6 | 54·4 | 37·4 | 27·9 | 20·0 |

TABLE III.

$L_4 = 12{\cdot}0''$, $l_1 = l_3 = 2{\cdot}0''$, $d_1 = 3{\cdot}0''$, $d_2 = 9{\cdot}0''$.

Pressures at

| $l_2$ | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 0·5″ | 76·5 | 66·7 | 61·7 | 60·0 | 57·8 | 33·5 | 23·3 |
| 1·0 | 76·9 | 67·9 | 63·9 | 60·2 | 56·8 | 33·5 | 23·1 |
| 1·5 | 76·9 | 68·2 | 65·2 | 60·0 | 55·0 | 33·4 | 22·5 |
| 2·0 | 77·3 | 69·7 | 67·4 | 60·0 | 53·1 | 32·8 | 22·1 |
| 3·0 | 79·0 | 72·1 | 71·1 | 60·9 | 49·5 | 31·2 | 21·5 |
| 4·0 | 79·4 | 75·0 | 73·9 | 58·3 | 45·7 | 30·3 | 21·0 |
| 5·0 | 82·3 | 77·3 | 76·7 | 58·0 | 41·4 | 28·3 | 19·7 |

TABLE IV.

$L_4 = 12{\cdot}0''$, $l_1 = l_3 = 2{\cdot}0''$, $d_1 = 1{\cdot}5''$, $d_2 = 10{\cdot}5''$.

Pressures at

| $l_2$ | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 0·5″ | 76·3 | 67·0 | 66·0 | 64·0 | 62·7 | 33·2 | 23·0 |
| 1·0 | 76·7 | 68·3 | 68·2 | 65·3 | 61·8 | 33·3 | 23·0 |
| 1·5 | 77·2 | 70·0 | 69·8 | 66·0 | 60·0 | 33·3 | 22·9 |
| 2·0 | 77·5 | 71·7 | 71·5 | 66·1 | 58·5 | 33·0 | 22·7 |
| 3·0 | 80·0 | 76·3 | 76·0 | 65·7 | 55·0 | 32·1 | 22·0 |
| 4·0 | 82·2 | 79·5 | 79·3 | 63·8 | 50·1 | 30·0 | 21·2 |
| 5·0 | 84·0 | 82·6 | 82·3 | 61·8 | 45·8 | 28·6 | 19·8 |

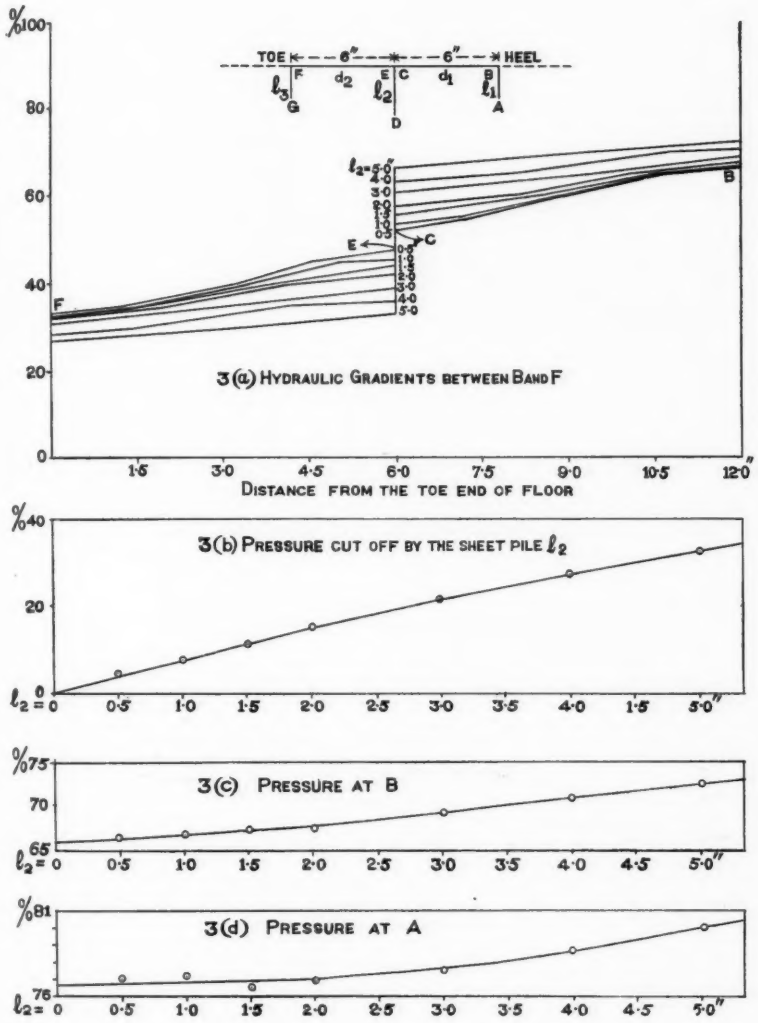
%
100
80
60
40
20
0
TOE
6"
6"
HEEL
F
E
C
B
G
D
A
$d_2$
$d_1$
$l_3$
$l_2$
$l_1$
$l_2$=5·0
4·0
3·0
2·5
2·0
1·5
1·0
0·5
0
3(a) HYDRAULIC GRADIENTS BETWEEN B AND F
1·5
3·0
4·5
6·0
7·5
9·0
10·5
12·0"
DISTANCE FROM THE TOE END OF FLOOR
%
40
20
0
3(b) PRESSURE CUT OFF BY THE SHEET PILE $l_2$
$l_2$ = 0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0"
%
75
70
65
3(c) PRESSURE AT B
$l_2$ = 0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0"
%
81
76
3(d) PRESSURE AT A
$l_2$ = 0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0"

FIG. 3.

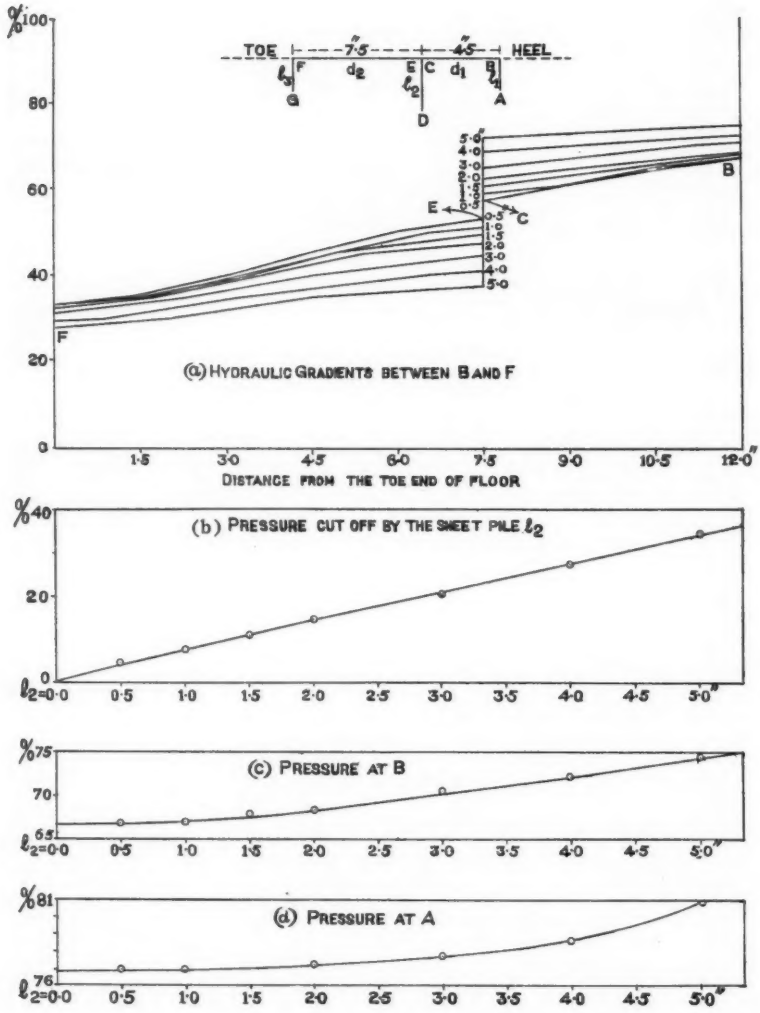
%
100
80
60
40
20
0
TOE
7·5
4·5
HEEL
F
G
E
D
C
A
B
5·0
4·0
3·0
2·0
1·5
1·0
0·5
(a) HYDRAULIC GRADIENTS BETWEEN B AND F
1·5
3·0
4·5
6·0
7·5
9·0
10·5
12·0"
DISTANCE FROM THE TOE END OF FLOOR
%40
20
0
(b) PRESSURE CUT OFF BY THE SHEET PILE $\ell_2$
$\ell_2$=0·0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0"
%75
70
65
(c) PRESSURE AT B
%81
76
(d) PRESSURE AT A

FIG. 4.

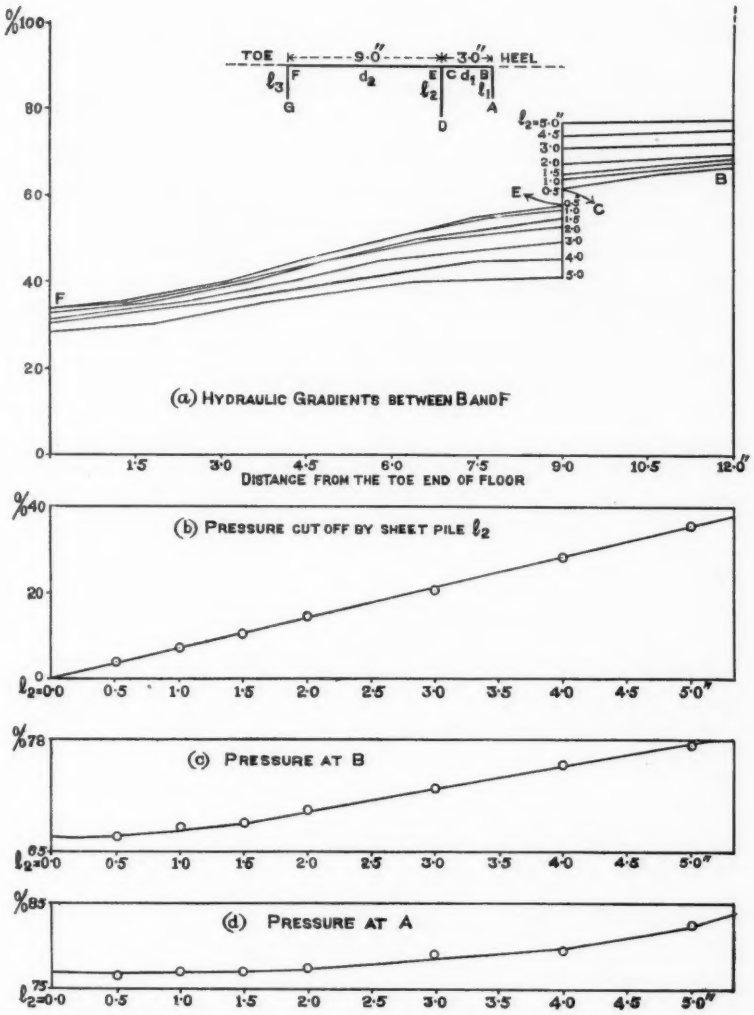
%100
80
60
40
20
0
TOE
9·0"
3·0"
HEEL
$l_3$
F
$d_2$
E
C
$d_1$
B
$l_1$
$l_2$
G
D
A
$l_2$=5·0"
4·5
3·0
2·0
1·5
1·0
·5
0
E
C
B
F
4·0
3·0
(a) HYDRAULIC GRADIENTS BETWEEN B AND F
1·5
3·0
4·5
6·0
7·5
9·0
10·5
12·0"
DISTANCE FROM THE TOE END OF FLOOR
%40
20
0
(b) PRESSURE CUT OFF BY SHEET PILE $l_2$
$l_2$=0·0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0"
%78
65
(c) PRESSURE AT B
%85
75
(d) PRESSURE AT A

FIG. 5.

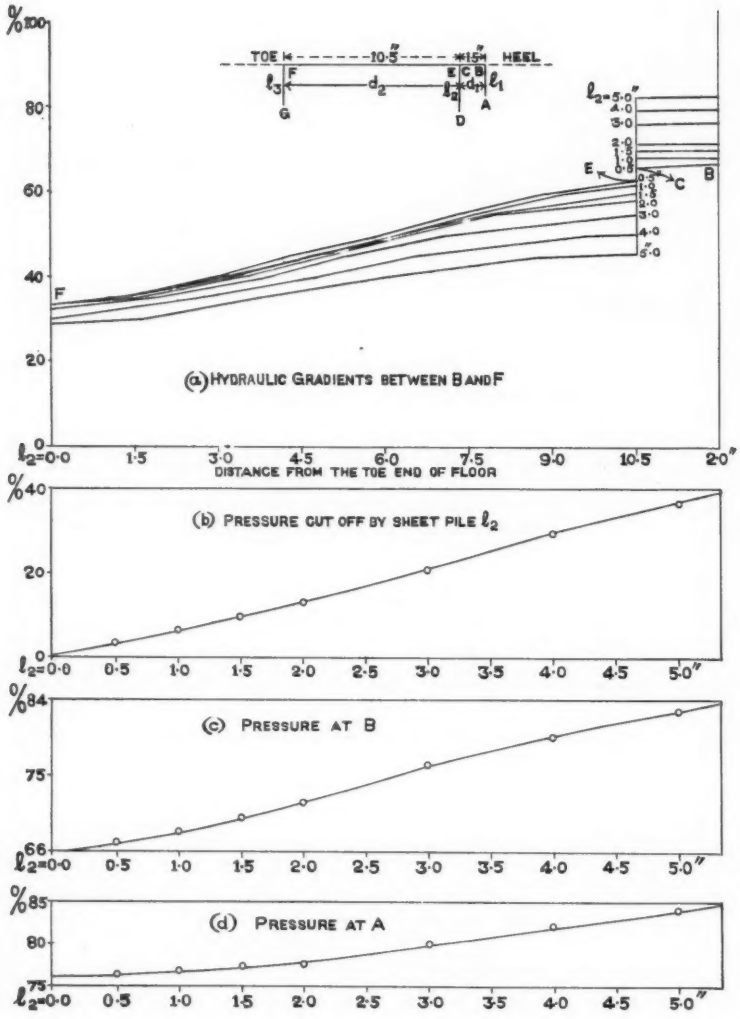
TOE
10·5"
1·5"
HEEL
F
E
C
B
A
G
D
$l_3$
$d_2$
$d_1$
$l_1$
$l_2$
(a) HYDRAULIC GRADIENTS BETWEEN B AND F
DISTANCE FROM THE TOE END OF FLOOR
(b) PRESSURE CUT OFF BY SHEET PILE $l_2$
(c) PRESSURE AT B
(d) PRESSURE AT A

FIG. 6.

Taking the case of Fig. 3, it will be seen that the intermediate sheet pile $l_2$ is fixed half way between the heel and the toe sheet piles. The difference of head acting at the heel and the toe is represented by 100. The distribution of pressure along the floor and sheet piles under the weir is shown for the case of $l_2 = 0 \cdot 5''$ by the curve B C E F in Fig. 3(*a*). The other curves in the figure are similarly plotted for the lengths $1 \cdot 0''$, $1 \cdot 5''$, $2 \cdot 0''$, $3 \cdot 0''$, $4 \cdot 0''$ and $5 \cdot 0''$ of the sheet pile.

The portions of the above curve such as E C along the ordinate show the pressures cut off by the intermediate sheet pile when its length is increased from $0''$ to $5 \cdot 0''$. This variation of pressure with respect to its length is plotted in Fig. 3(*b*) which thus gives the law of variation of pressure in relation to the length of the intermediate sheet pile.

Figs. 3(*c*) and 3(*d*) show the variation of pressure at the points B and A (Fig. 1) respectively, when the length of $l_2$ changes from $0''$ to $5 \cdot 0''$.

As will be seen from Fig. 3(*c*) the slope of the curve is small to begin with, but shows an increase when the length of the intermediate sheet pile exceeds $2''$ in the model, *i.e.*, exceeds the length of the sheet piles at the two ends of the floor. This means that when the intermediate pile is longer than the piles at the end, it becomes more effective in reducing pressure than when its length is smaller than that of either of the piles at the end.

Fig. 3(*d*) shows the variation of the pressure at A when the length of the intermediate sheet pile increases gradually from $0''$ to $5 \cdot 0''$. The variation of the pressures at A is similar in nature to that at B. As mentioned above the slope of the curve is small to begin with, but increases when the length of the intermediate pile exceeds $2''$ in the model.

Figs. 4, 5 and 6 show in a similar way the hydraulic gradients for cases in which the intermediate sheet pile is $4 \cdot 5''$, $3 \cdot 0''$ and $1 \cdot 5''$ respectively from the sheet pile at the heel.

So far as the changes of pressures at B and A are concerned, the effects appear to be of a similar nature to that in Fig. 3 when the position of the intermediate sheet pile is changed as in Figs. 4, 5 and 6.

The pressure cut off by the intermediate pile itself, when its length and position are changed is shown in Table V.

It will be seen from Table V, that when the length of the intermediate pile $l_2$ is two inches or less, the pressure cut off by it decreases gradually when it is moved from the centre towards the heel sheet pile. On the other hand, when $l_2$ is longer than $2 \cdot 0''$ the pressure cut off by it increases gradually when it is shifted from the centre towards the sheet pile at the heel. It may be noted that the heel and the toe sheet piles are two inches in all these cases.

TABLE V.

| Distance of the intermediate sheet pile from the toe end | Percentage pressure cut off by $l_2$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | $l_2 = 0{\cdot}5''$ | $1{\cdot}0''$ | $1{\cdot}5''$ | $2{\cdot}0''$ | $3{\cdot}0''$ | $4{\cdot}0''$ | $5{\cdot}0''$ |
| $6{\cdot}0''$ | 4·5 | 7·8 | 11·7 | 15·2 | 20·0 | 27·3 | 32·5 |
| 7·5 | 4·2 | 7·7 | 10·8 | 14·6 | 20·3 | 27·6 | 34·2 |
| 9·0 | 3·9 | 7·1 | 10·2 | 14·3 | 20·6 | 28·2 | 35·3 |
| 10·5 | 3·3 | 6·4 | 9·8 | 13·0 | 21·3 | 29·2 | 36·5 |

Thus in designing a weir, if the intermediate sheet pile is of about the same length as the end sheet piles or is shorter, it should be placed as near the centre as possible if it is to exert its maximum effect in reducing pressure. On the contrary if it is longer than the end sheet pile, it should be placed nearer to the heel sheet pile, for producing maximum effect in reducing pressure.

*Design of a Weir with Three Sheet Piles.*—The twentyeight cases investigated here are such as to cover the ordinary designs, so that in many cases one or the other set will be found to readily fit in with the design in question. In cases where it does not, the results obtained in the investigation can be applied to determine the uplift pressures under any weir with three sheet piles.

For example, let us take a weir with the following dimensions and determine the uplift pressures employing the graphs and tables given in the paper :

Length of floor (L) .. .. .. = 150 ft.
Length of sheet piles at heel and toe ($l_1$ and $l_3$) .. .. .. .. = 18 ft.
Length of the intermediate sheet pile .. = 25 ft.
Distance between the heel and the intermediate sheet pile .. .. .. = 50 ft.

Since the Law of Similarity holds good in models, the projection of the model to any prototype will yield identical results of uplift pressures. The dimensions of the prototype can thus be reduced for purposes of calculation to those shown in Fig. 7. The scale of reduction in this case is 1/150.

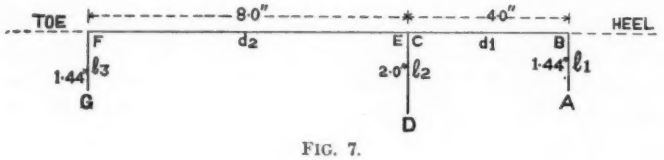


FIG. 7.

Referring to Fig. 7 and to Table II, it will be seen that the pressure at G varies from 22·8 to 22·1 when the length of the intermediate sheet pile changes from 0 to 3·0″. This change being small, the effect of the central sheet pile on the variations of pressures at F and G may be considered negligible in practical cases. So far as the pressures at G and F are concerned, this reduces, therefore, to the case of two sheet piles at the ends of a floor. These pressures are 21·5 and 30·4 at G and F respectively.*

To find the pressure at E, the following method may be adopted :—

It will be seen from Table I that when the sheet pile $l_2$ is 2″ long and is fixed exactly in the centre of the floor, the pressure at E is 42·3 per cent. The pressure at E increases as the intermediate sheet pile is shifted towards the heel end. The values of pressures at E for $d_2 = 7·5''$, $9·0''$ and $10·5''$ are found from Tables II, III and IV to be 47·7, 53·1 and 58·5 per cent. respectively. By interpolation the value of pressure at E when $l_2$ is $8·0''$ from the toe is found to be 49·5 per cent. The pressures at D and C, similarly obtained, are 56·8 and 63·8 per cent. respectively.

The determination of pressures at B and A offers some difficulty, as the influence of the intermediate sheet pile $l_2$ which is near the heel-pile has to be taken into account. If the sheet pile $l_2$ were removed altogether, the pressures at B and A would be 69·6 and 78·5 per cent. respectively as has been shown from the simple case of two equal sheet piles (1·44″) at the ends of a 12″ floor.[4]

The dimensions of the two sheet piles $l_2$ and $l_1$ in question are $2·0''$ and $1·44''$ respectively. The case corresponds to that of the sheet piles $l_2$ and $l_1$ equal to $2·8''$ and $2·0''$ respectively which has been investigated, the ratio of $l_2$ to $l_1$ in both cases being the same.

By plotting suitable curves from the Tables I–IV, the following values of pressures at A and B can be obtained when $l_1 = 2·0''$, $l_2 = 2·8''$ and $d_2 = 8·0''$. The pressures thus obtained at A and B are :—

| | A. | B. |
|---|---|---|
| $l_2 = 0·0''$ .. | 76·1 | 66·2 |
| $l_2 = 2·8''$ .. | 77·7 | 70·3 |

These values give the change in pressures at A and B when a $2·8''$ sheet pile is introduced at a point $8·0''$ from the toe.

It has already been observed that the pressures at A and B are 78·5 and 69·6 per cent. respectively when $l_1 = 1·44''$ and there is no intermediate

* These pressures have been read off from the curves in Fig. 2 of the paper on "Uplift Pressure and Design of Weirs with Two Sheet Piles", *Proceedings of the Indian Academy of Sciences*, 1936, Vol. IV, p. 147.

sheet pile. These values would increase in the ratios 77·7/76·1 and 70·3/66·2 respectively when a 2″ sheet pile is introduced at 8·0″ from the toe end. The values thus obtained are 80·2 and 73·9 per cent. respectively.

In order to verify the results obtained by the graphical method described above, a model of this design was tested experimentally in the electrical tray. The results obtained by the two methods are given below for comparison :

| | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| Experimental Method .. | 79·9 | 71·9 | 64·9 | 56·4 | 47·9 | 28·8 | 20·8 |
| Graphical Method .. | 80·2 | 73·9 | 63·8 | 56·8 | 49·5 | 30·4 | 21·5 |

It can be seen from the foregoing discussion that though the graphical method of obtaining the uplift pressures under the floor is not rigorous, it leads to results within two per cent. of the experimental value. In the design of actual works, this accuracy is quite sufficient, as there are other factors causing variations in uplift pressures which cannot be determined to this degree of accuracy.

When a doubt arises as to the correctness of the design by the graphical method or by other empirical equations derived from the graphs, it can be referred to experiment which can be carried out in a laboratory.

*Summary.*

In this investigation, the uplift pressures under weirs with three sheet piles have been determined. By studying the effect of varying the length and position of the intermediate sheet pile, working rules have been obtained for the design of weirs with three sheet piles.

We have great pleasure in thanking Dr. E. McKenzie Taylor, the Director, for the keen interest he took in this problem.

REFERENCES.

1. Gurdas Ram, V. I. Vaidhianathan and E. McKenzie Taylor, *Proc. Ind. Acad. Sci.*, 1935, **2**, 22.
2. V. I. Vaidhianathan and Gurdas Ram, *Punjab Irrigation Research Institute, Research Publication*, 1935, **5**, No. 4.
3. V. I. Vaidhianathan, Gurdas Ram and E. McKenzie Taylor, *Proc. Ind. Acad. Sci.*, 1935, **2**, 646.
4. Gurdas Ram and V. I. Vaidhianathan, *Proc. Ind. Acad. Sci.*, 1936, **4**, 147.

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